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INVESTIGATIONS CONCERNING PROBABLE IMPACT OF NITRILOTRIACETIC ACID ON GROUND WATER

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The fate and effect of NTA both in ground waters and in soil profiles overlying ground waters were studied using laboratory models. Sorption of NTA on soils slows its movement into and through ground waters. Sorption is not sufficient to prevent or greatly reduce potential pollution of ground water by NTA used as a detergent builder. NTA infiltrating through most unsaturated soils undergoes rapid and complete degradation and contributes only inorganic nitrogen compounds and carbonate to ground waters. NTA infiltrating through saturated soils experiences only very limited degradation, with a major portion entering ground water intact. Any NTA which escaped degradation during infiltration through soils could transport such metals as iron, zinc, chromium, lead, cadmium, and mercury from soils into ground waters. NTA would degrade slowly in essentially anaerobic ground-water environments, with production of CO2, CH4, and possibly other organic compounds. (Knapp-USGS)

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INVESTIGATIONS CONCERNING PROBABLE IMPACT OF NITRILOTRIACETIC ACID ON GROUND WATERS

by

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ABSTRACT

Laboratory studies were employed to investigate the fate and effect of NTA both in ground waters and in soil profiles overlying ground waters.

Studies of the sorption of NTA by sand, loam, and clay-loam soils indicated that sorption of NTA on soils could slow its movement into and through ground waters. Sorption will probably not be sufficient to prevent or greatly reduce potential pollution of ground water by NTA used as a detergent builder.

Soil column studies were employed to investigate the degradation and effect on metals of NTA infiltrating through soils. These studies indicated: NTA infiltrating through most unsaturated soils likely would undergo rapid and complete degradation and contribute only inorganic nitrogen compounds and carbonate to ground waters; NTA infiltrating through saturated soils would probably experience only very limited degradation, with a major portion entering ground water intact; any NTA which escaped degradation during infiltration through soils could transport such metals as iron, zinc, chromium, lead, cadmium, and mercury from soils into ground waters.

Studies with model aquifers constructed from natural aquifer sand indicated that NTA would likely undergo slow degradation in essentially anaerobic ground-water environments, with production of CO_2, CH_4, and possibly other organic compounds.

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SECTION I

CONCLUSIONS

The investigations described in this report permit the following conclusions concerning the potential impact of NTA on ground water.

1. Sorption of NTA by some types of soils may considerably slow the initial movement of this compound into and through ground waters. However, sorption of NTA by soils does not appear to be sufficient to prevent or appreciably decrease the pollution of ground waters by this compound over the course of its long-term usage as a detergent builder.

2. NTA infiltrating through unsaturated soils, as in properly operating septic tank percolation fields, will probably undergo rapid and complete degradation. Only inorganic nitrogen compounds and carbonates are likely to enter ground water as the result of such degradation. Introduction of these substances into ground waters is not desirable, but the quantities introduced as a result of NTA use in detergent are not likely to be sufficient to create critical pollution problems.

3. The degradation of NTA infiltrating through unsaturated soils which contain high levels of heavy metals, such as those receiving wastes from metal plating operations, may be partially inhibited as a result of toxicity of the metals to soil microorganisms; hence, some NTA may enter ground water under such circumstances.

4. NTA infiltrating through saturated soil systems, as in flooded septic tank percolation fields and under some waste water lagoons, will likely undergo only limited degradation; hence, a significant portion will enter underlying ground water, possibly accompanied by small quantities of organic degradation products of NTA.

5. NTA which reaches the water table will likely undergo slow degradation in the essentially anaerobic ground-water environment. The final products of such degradation will probably include carbon dioxide and methane, and possibly other organic compounds of low molecular weight and relatively high volatility. Unknown intermediate products of NTA degradation may also be present in an aquifer when NTA is being actively degraded.

6. NTA that infiltrates through overlying soil into ground water without being degraded may solubilize and transport into the ground water such metals as iron, zinc, chromium, lead, cadmium, and mercury which may be present in the soil. Situations where NTA might infiltrate through soils receiving wastes containing high levels of toxic heavy metals, such as metal plating wastes, would appear to entail consderable potential for metals contamination of underlying ground waters. However, comprehensive evaluation of the potential threat to ground-water quality posed by solubilization and transport of metals in soils by infiltrating NTA will require further elucidation of the factors controlling formation of NTA-metals chelates in soils.

7. Even in the most favorable circumstances, use of NTA as a detergent builder is likely to result in some increases in nitrogen and probably carbon in ground waters. Phosphates in waste waters do not readily move into or through ground waters because of strong sorption in soils. Hence, in comparison to phosphates the use of NTA in detergents would likely result in at least a limited adverse impact on ground water.

SECTION II

RECOMMENDATIONS

On the basis of this research, it is recommended that additional investigations be conducted to further elucidate specific questions concerning the probable impact of NTA on ground water before unlimited use of this compound in detergent is begun.

Obviously, the effect of NTA which enters ground waters used as domestic water supplies on the health of consumers of such ground water must be determined.

The potential for transport of metals from soils into ground waters by NTA should be unequivocally established. This will require thorough investigation of the complex factors affecting the formation of chelates by NTA and metals in soils, including both metals native to the soils and those deposited to soils by waste disposal activities. The possibility of initial solubilization of soil metals by infiltrating NTA, with the metals remaining in solution after degradation of the NTA, should also receive attention.

Should limited use of NTA in detergents coupled with strict environmental monitoring be approved for further evaluation of the acceptability of this substance, careful and comprehensive monitoring of NTA and metals concentrations should be conducted at a number of selected sites where transport of metals into ground water by infiltrating NTA appears most likely to occur.

The pathway of anaerobic degradation of NTA in ground-water environments should be elucidated, with identification of intermediate products of degradation and determination of the extent to which these intermediates are likely to be present during such degradation. Should the nature and quantities of degradation products merit sufficient concern, the mammalian toxicities of these compounds should also be determined. The extent of NTA degradation in the presence of relatively large quantities of other degradable organic compounds in essentially anaerobic ground-water environments should also be the object of further study.

Additional research should consider the possible occurrence during successive infiltration of NTA through partially saturated and fully saturated soils of partial, or arrested aerobic degradation, with concommitant appearance in the water infiltrating to ground water of intermediate products of NTA degradation, such as iminodiacetic acid.

SECTION III

INTRODUCTION

Modern synthetic detergents, which commonly contain 40-50 percent condensed phosphates, are estimated to contribute more than two-thirds of the phosphorus load of waste waters in the United States.[1] Since phosphorus in waste waters is believed to be a major factor in the cultural eutrophication problem now plaguing many of our surface waters, there is currently a considerable expenditure of effort and resources by both industry and government directed toward the reduction or elimination of the phosphate content of detergents. However, the condensed phosphates (known as builders) used in detergent formulation contribute significantly to detergent performance by complexing calcium, magnesium, and other metallic ions in wash waters which otherwise would attenuate or destroy the surfactant power of the detergent. Therefore, in order to maintain detergent performance at anywhere near presently accepted levels and yet achieve the goal of reduction or elimination of phosphates in detergents, it is likely that an environmentally acceptable replacement for the condensed phosphate detergent builders must be developed. The leading candidate thus far proposed for this purpose is nitrilotriacetic acid (Figure 1), a member of a group of amino-carboxylic acids long known as exceptionally efficient chelating agents.

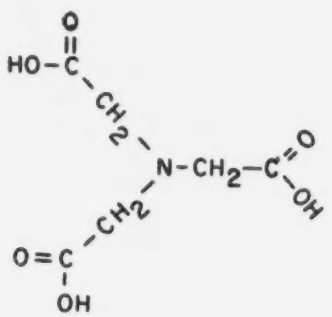

FIGURE 1. NITRILOTRIACETIC ACID

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Nitrilotriacetic acid (hereafter called NTA) is an organic compound containing no phosphorus; hence, its use in detergents as a replacement for a significant portion of the condensed phosphate builders would be expected to proportionately decrease the aquatic phosphorus problem. By virtue of its ability as a chelating agent, NTA fulfills the major functional requirement for a detergent builder since, in a properly buffered detergent solution, it effectively complexes the troublesome metallic ions capable of adversely affecting detergent performance. Also, a process is available which permits the production of NTA in highly pure form (as the sodium salt) at a cost and in quantities required for the large scale use of this compound in detergents.

There are, however, considerations other than the phosphorus problem regarding the environmental acceptability of NTA. Although microorganisms found in sewage treatment systems have been shown capable, under proper conditions, of degrading NTA to end products of water, carbon dioxide, and nitrate,[2,3,4] the extent and pathways of NTA degradation in various aquatic environments, the toxicity of the parent compound and possible organic products of its degradation, and the effect of NTA on the solubility and transport of metals in aqueous environments have not been clearly defined. Hence, valid questions exist concerning the impact on water resources of large scale employment of NTA in detergents, both from the standpoint of ecological effects and human health. The magnitude of the potential input of NTA to waste waters, which would amount to over a billion pounds annually were NTA to replace only half of the condensed phosphates currently utilized in detergents in the United States, requires that these questions be carefully evaluated before final designation of NTA as a suitable replacement for the phosphate builders in detergents.

Among the major questions regarding the environmental acceptability of NTA as a detergent builder are those concerning the potential effects of NTA on ground-water resources. Ground waters were estimated to provide approximately 23 percent of all fresh water and about 33 percent of public water supplies in the United States in 1965.[5] Also, in many areas ground waters constitute valuable reserves of fresh water which are now used only in emergencies or are as yet relatively untapped. Protection of these valuable resources from pollution is particularly important because pollution effects almost invariably persist much longer and are more difficult to eradicate in ground waters than in surface waters.

In considering the potential effects of NTA on ground-water resources, it is necessary first to examine the pathways by which NTA might enter ground water. These pathways are restricted essentially to two possibilities: infiltration through the soil mantle above the water table and discharge directly into the ground water. The first pathway would be operative in cases where waters containing NTA are discharged to permeable soils appreciably above the water table, such as in properly designed and operating septic systems, waste lagoons, and related sewage spreading systems. The second pathway would be followed in the all too frequent situations where septic systems, lagoons, and similar waste disposal systems are connected directly to ground waters, and also in cases of direct artificial recharge of aquifers.

NTA infiltrating through the soil mantle above the water table would be subject to possible sorption on soil particles, degradation, and reaction with metal ions to form soluble metal chelates. NTA reaching the water table, whether by direct introduction to ground water or after infiltrating through the overlying soil, would be subject to analogous phenomena within the ground-water environment, where conditions of low oxygen tension ordinarily prevail.

These environmental possibilities necessitate that the following specific questions be answered in order to assess the probable impact on ground water of large scale use of NTA in detergents.

1. How will sorption affect the infiltration of NTA through soil profiles and its movement within ground-water aquifers?

2. To what extent will NTA be degraded during infiltration through unsaturated and saturated soils and within essentially anaerobic ground-water environments?

3. If NTA is degraded during infiltration through soil profiles or within ground-water environments, what will be the nature and fate of the degradation products?

4. To what extent will NTA affect the transport of metals into and through ground water?

This report describes a research project undertaken in an effort to provide answers to these questions. Time limitations dictated that the project be relatively short term, and research was therefore limited to a rather intensive laboratory investigation consisting of three phases which were conducted more or less concurrently.

The first phase of the investigation was concerned with the effect of sorption on the infiltration of NTA through the soil mantle and its movement through ground water. This involved determination of sorption isotherms for NTA on typical sand, loam, and clay-loam soils.

In the second phase of the research effort, soil columns were employed for studies pertaining to the fate of NTA infiltrating through the soil mantle and effects of NTA on metals transport in ground water. Initially, columns containing typical sand, loam, and clay-loam soils were utilized to investigate the possible degradation of NTA during infiltration through both unsaturated and saturated soils and the effects of NTA on the solubility and transport of metals native to the soils. Subsequently, columns containing sand enriched with heavy metals were utilized for the principal purpose of examining further the question of possible transport of metals into ground water by NTA.

The third phase of the project involved the use of simulated aquifers constructed in the laboratory from natural aquifer sand for investigation of the possible degradation of NTA in an essentially anaerobic ground-water environment.

SECTION IV

MATERIALS AND METHODS

Sorption Studies

Sorption isotherms were determined for NTA on a sand, a loam, and a clay-loam soil in order to broadly span the various soil types which might be encountered in natural situations. The soils used, all of which were obtained in the vicinity of Ada, Oklahoma, were identified by United States Department of Agriculture Soil Conservation Service soil surveys as Konawa loamy fine sand, Claremore loam, and Burleson clay loam. Soils were air dried and screened to remove pebbles, seeds, and similar extraneous matter before use.

Solutions of the trisodium salt of NTA (NTA Na_3) uniformly labeled with carbon-14 were utilized in sorption studies as well as the other phases of this investigation. These solutions were prepared from ^{14}C-NTA, uniformly labeled, specific activity 2.5 mCi/mmole (New England Nuclear Corporation, 575 Albany Street, Boston, Massachusetts) mixed with proper proportions of unlabeled NTA $Na_3 \cdot H_2O$ (NTA Batch No. 1, supplied by the Soap and Detergent Association, 485 Madison Avenue, New York, New York) to give the desired activity and NTA Na_3 concentration. Stock solutions of NTA Na_3 were sterilized by filtering through 0.45 μ Millipore filters and aseptic techniques were employed throughout the sorption studies to eliminate the possibility of microbial degradation of NTA.

For determination of quantities of NTA sorbed by the soils in contact with NTA solutions, 2 g portions of soil were carefully weighed into individual 500 ml Erlynmeyer flasks stoppered with polyurethane plugs. Flasks and contents were sterilized by autoclaving for 15 minutes at 121°C. A 100 ml aliquot of sterile aqueous ^{14}C-NTA Na_3 solution containing 2, 10, or 40 mg/l NTA Na_3 was added aseptically to each flask. Blank flasks containing aliquots of the same NTA Na_3 solutions but no soil were similarly prepared.

Both blank flasks and those containing soil were agitated on a rotary shaker at 20°C. Periodically, flasks were removed from the shaker for approximately 15 minutes to allow soil solids to settle, and a 2 ml sample of the aqueous phase was removed aseptically from each flask. These samples were centrifuged to remove suspended matter. Levels of radioactivity, and hence NTA Na_3, in the centrifugates were determined by means of a Beckman LS-150 liquid scintillation spectrometer, employing 1.5 ml of centrifugate in 16 ml of toluene scintillation cocktail containing 8.0 g/l Butyl PBD and 0.5 g/l PBBO.

When maximum sorption of NTA Na_3 on soil particles had occurred as indicated by attainment of constant NTA Na_3 concentrations in the aqueous phases of the soil flasks, the quantities of NTA Na_3 sorbed per gram of soil at the observed equilibrium concentrations were determined from the following relationship.

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$$\text{NTA } Na_3 \text{ Sorbed/g Soil} = \frac{\text{Total NTA } Na_3 \text{ in 100 ml of solution in blank flask} - \left[\text{Total NTA } Na_3 \text{ in liquid phase of soil flask at equilibrium} + \text{Total NTA } Na_3 \text{ removed from soil flask during sampling}\right]}{2}$$

Values thus obtained were utilized for construction of sorption isotherms.

Soil Column Studies

Studies Employing Natural Soils

Initial soil column studies were concerned with the possible degradation of NTA during infiltration through unsaturated and saturated sand, loam, and clay-loam soils and the effect of NTA on metals native to these soils.

The soils employed were those used in the previously described sorption studies, namely Konawa loamy fine sand, Claremore loam, and Burleson clay loam. These soils were packed into 10.2 cm O.D. x 117 cm borosilicate glass columns equipped with 1 cm O.D. outlets. Plugs of glass wool topped by 2.5-4 cm of pea gravel served as supports for the soils in the columns.

For preparation of sand and loam columns, soil was added to the column in small increments sufficient to increase the column height 5-8 cm, and the column contents were prodded with a metal rod after each addition to insure uniformity of packing. However, preparation of clay loam columns by this procedure was unsatisfactory because of very low rates of liquid flow through the columns obtained. Clay-loam columns were therefore prepared by first screening the soil to obtain an 8-70 mesh cut of soil particles and then adding this material incrementally to the columns, employing vibration to obtain relatively uniform packing. Two columns of each soil type were prepared, with exactly equal weights of soil being utilized for preparation of both columns of a given type. Columns of soil were 9.5 cm in diameter and averaged 99 cm in height. Additional descriptive data for the columns are given in Table 1.

Table 1

Weight and Volume Data for Soil Columns

Column	Weight Soil (g)	Water Required To Fill Column To Top of Soil (ml)	Water Drained by Gravity (ml)
Konawa Loamy Fine Sand	11,460	2,170	1,300
Konawa Loamy Fine Sand	11,460	2,110	1,280
Claremore Loam	8,780	3,260	1,285
Claremore Loam	8,780	3,045	1,165
Burleson Clay Loam	9,630	3,490	*
Burleson Clay Loam	9,630	3,540	*

*Data not obtained.

One column of each soil type was operated under unsaturated, or aerobic, conditions with the water table near the bottom of the column, while the other column of the pair was operated under saturated, or essentially anaerobic, conditions by maintaining the water table near the surface of the soil. Columns were operated at room temperature (usually 22-25°C) in a darkened fume hood. The loam and clay-loam columns used in these studies are pictured in Figure 2.

Columns were dosed daily for 58 days at a hydraulic loading of 2 gal/ft^2 (580 ml/day for each column) with a weak synthetic sewage prepared from the liquid diet food Sego (Pet, Incorporated, Saint Louis, Missouri; BOD approximately 163,000 mg/l), ^{14}C labeled NTA Na_3, and distilled water. This synthetic sewage, which contained approximately 50 mg/l both of BOD and NTA Na_3 and had a specific activity of 900 pCi/ml, was fed to the columns at a rate of 2 ml/min during a daily dosing period of approximately 5 hours by means of a Technicon proportioning pump (Technicon Corporation, Tarrytown, New York). Sterile synthetic sewage was prepared fresh daily and feed lines were washed thoroughly with detergent and flushed with 95 percent ethanol after each dosing in order to minimize the possibility of NTA degradation occurring before the synthetic sewage entered the columns.

Upon completion of the initial 58 days of operation, dosing of the soil columns was continued by essentially the same procedure for 19 additional days, except that no NTA was added to the synthetic sewage.

Column effluents were analyzed daily for NTA Na_3, radioactive carbon and pH.

NTA Na_3 was determined by an automated zinc-zincon procedure which was essentially that of Thompson and Duthie,[2] except that a 6 mm O.D. x 56 cm tube packed with 20-50 mesh Amberlite IR-120 ion exchange resin (H^+ form) was inserted in the system between the sampling and mixing stages to remove cations likely to interfere with the analysis. Radioactive carbon was determined by the previously described liquid scintillation spectrometry procedure employed in the sorption studies.

Selected effluents were also subjected to thin layer chromatography and radioautography in an effort to detect intermediate organic degradation products of NTA. Ten milliliter effluent samples were concentrated under vacuum in rotary evaporators, and 50 µl aliquots of the concentrate were chromatographed with standard samples of NTA and some possible NTA degradation products including: N-methyliminodiacetic acid; iminodiacetic acid; N,N-dimethylglycine; glycine; and trimethylamine. Thin layer chromatography systems employed were: Avicel SF microcrystalline cellulose as stationary phase and either tertiary butyl alcohol-formic acid-water (40:10:16, called tBFW) or phenol-water (3:1) as mobile phase; and, a mixture of 20 percent Amberlite CG-400 anion exchange resin-80 percent Avicel SF as stationary phase with either tBFW or 0.15 N sodium chloride as mobile phase. R_f values obtained with these systems are presented in Table 2.

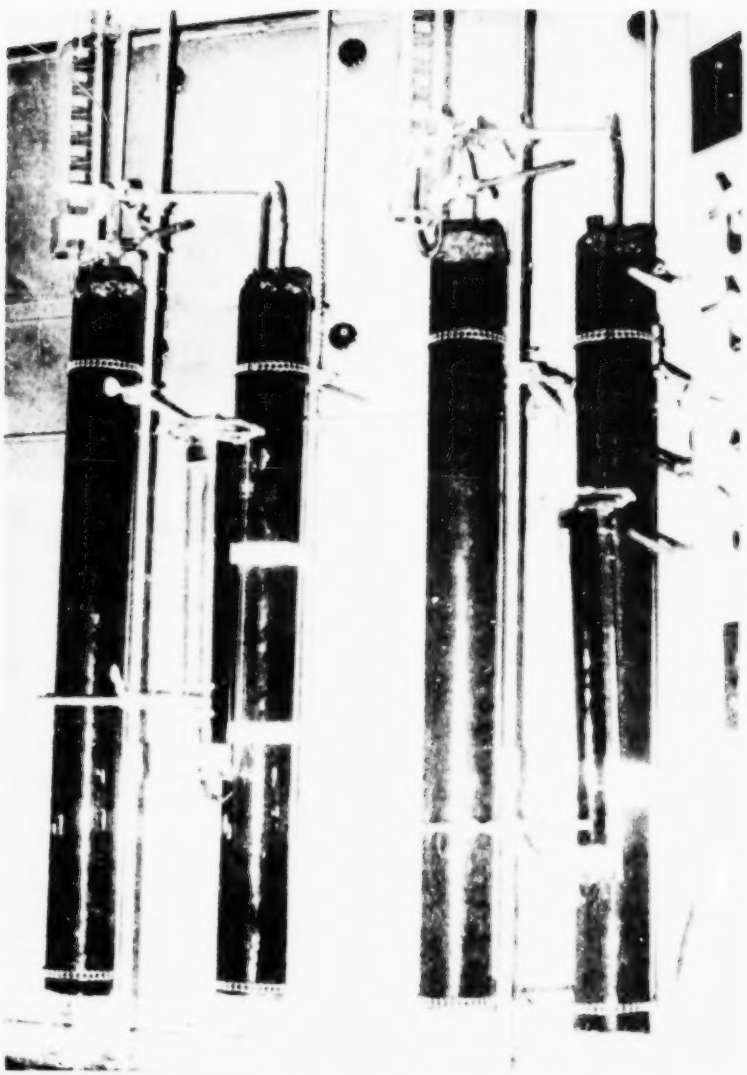

FIGURE 2. LOAM AND CLAY LOAM
SOIL COLUMNS

Table 2

R_f Values of NTA and Some Postulated NTA Degradation Products

Compound	Stationary Phase: Avicel SF, MP 1	Avicel SF, MP 2	20% Amberlite CG-400 80% Avicel SF, MP 1	20% Amberlite CG-400 80% Avicel SF, MP 3
Nitrilotriacetic Acid	0.41	0.31	0.33	0.38
N-Methyliminodiacetic Acid	0.44	0.58	0.42	0.90
Iminodiacetic Acid	0.37	0.31	0.35	0.82
N,N-Dimethylglycine	0.54	0.91	0.48	0.92
Trimethylamine	0.55	0.88	0.57	0.93
Glycine	0.44	0.37	0.38	0.87

Mobile Phases:
- MP 1 t-butyl alcohol-formic acid-water (40:10:16)
- MP 2 phenol-water (3:1)
- MP 3 0.15 N sodium chloride

The system of 20 percent CG-400 resin-80 percent Avicel SF with 0.15 N NaCl was most used in this work because it was less affected than the other systems by substance in the effluent concentrates which tended to interfere with migration of NTA and NTA degradation products on the chromatograms and also because it gave significant separation between NTA and the possible degradation products studied, although the latter compounds were not individually differentiated.

Developed chromatograms were placed in contact with Kodak No-Screen Medical X-Ray film for 22-24 days to obtain radioautograms. After radioautography chromatograms were sprayed with chromogenic reagents to visualize the standard compounds in order that radioautograms and chromatograms could be compared. The visualization process involved spraying with 0.01 percent zinc sulfate in methanol, drying the plate while exposing it to ammonia fumes, spraying with 0.1 percent zincon (2-carboxy-2'-hydroxy-5'-sulfoformazylbenzene) in ethanol, and again drying the plate in ammonia fumes. By this procedure, NTA and the possible NTA degradation products studied were visualized as rosy pink spots on a blue background. As little as 0.5 µg NTA produced visible spots on chromatograms, but much larger quantities of N,N-dimethylglycine and trimethylamine were required for detection.

In order to determine the extent of carbon dioxide production resulting from degradation in the columns of NTA labeled with ^{14}C, $^{14}CO_2$ was determined in selected effluents. For this determination, aliquots of effluent samples were acidified with 0.1 N hydrochloric acid and the acidified samples were then purged with nitrogen gas. The purge gas from each sample was passed through a CO_2 scavenger solution consisting of 2-ethoxyethanol and 2-ethanolamine (8:1), and the activity of the scavenger solution was then determined by liquid scintillation spectrometry.

Column effluents were also analyzed for selected metals in an effort to discern effects of NTA on solubility and transport of metals native to the soils used in the columns.

Emission spectrograms were first obtained from effluents produced at the beginning of the study, when no NTA was passing through the columns, and from effluents produced after NTA or its degradation products began to elute from the columns, as indicated by radioactivity of the effluents. This involved ten-fold evaporative concentration of the effluent samples, followed by analysis of the concentrates by means of a Jarrell-Ash Mark IV Ebert convertible plane grating spectrograph, employing the rotating disc attachment for sampling and a high voltage spark for excitation. The spectrograms thus obtained were compared semi-quantitatively to detect those metals appearing to increase significantly in concentration as NTA concentrations in the effluents increased. These metals (iron, manganese, zinc, nickel, and cobalt) were then quantitatively determined by atomic absorption spectrophotometry in effluents obtained throughout the study, employing a Perkin Elmer Model 403 atomic absorption spectrophotometer and standardized analytical procedure.(6)

Studies Employing Sand Enriched with Metals

Upon completion of the initial soil column studies, additional studies of a similar nature were begun with the principal objective of gaining further information concerning the possible transport of metals into ground water by NTA. For these studies soil columns 9.5 cm in diameter and approximately 99 cm in height were prepared from Konawa loamy fine sand enriched with lead, zinc, chromium, cadmium, and mercury.

All columns were initially packed to a depth of approximately 35 cm with loamy fine sand containing no additive, employing the same packing procedures as used for preparation of the sand and loam columns employed in the initial soil column studies. Enriching materials were then thoroughly mixed with sufficient additional sand to provide a total weight of 11,460 g of soil in each column, and packing of the columns was completed with these enriched soils.

Two columns were prepared from sand enriched with the following natural ores (obtained from Burminco Rocks and Minerals, 128 Encinitas, Monrovia, California): galena (PbS); sphalerite (ZnS); chromite ($Fe(CrO_2)_2$); greenockite (CdS); and cinnabar (HgS). These ores were ground to insure homogenity, analyzed to determine actual metal content, and then added to the sand matrix in sufficient quantities that the individual packed column would contain 5 g of each of the five metals except chromium. Available quantities of chromite, which contained only 0.1 percent chromium, were sufficient to provide only 995 mg of this metal per column.

The other four columns were packed from sand enriched principally with a synthetic sludge prepared from a solution of soluble salts of lead, cadmium, chromium, and zinc. The metals were precipitated by adjusting the solution to pH 10 with sodium hydroxide, and the resulting sludge was collected by

centrifugation, dried, and ground to a powder. This material, supplemented with mercuric sulfide (cinnabar) as a source of mercury, was mixed with sand in such quantity that the individual packed column would contain 5 g of each of the five metals.

Two of the columns containing synthetic sludge were operated under unsaturated, or aerobic, conditions, while the other pair of sludge-containing columns and the two columns containing the ores were operated under saturated, or essentially anaerobic, conditions. In order to further eliminate possible aerobic zones in the tops of saturated columns, a blanket of nitrogen was maintained over these columns at all times.

The columns were dosed daily at a hydraulic loading of 2 gal/ft^2 (580 ml/day for each column). One column of each pair (unsaturated sludge, saturated sludge, and saturated ore) was dosed with 67 mg/l of ^{14}C labeled NTA Na_3 in distilled water (specific activity 920 pCi/ml). The second column of each pair served as a control and was dosed with distilled water only. The same precautions as used in the initial soil column studies were employed in this work to prevent significant microbial activity in the feeds until they had entered the column. In order to assess the effects of an additional carbon source on the parameters of interest, sufficient Sego to impart a BOD of 50 mg/l was added to the daily feed solutions starting with the 56th and 53rd day of operation, respectively, for the columns dosed with NTA and the control columns. The columns were operated for a total of 92 days.

Effluents from columns dosed with NTA Na_3 were analyzed for NTA Na_3 by the automated zinc-zincon method, for radioactive carbon by liquid scintillation spectrometry, and for pH in the same manner as in the initial soil column studies. Iron, manganese, lead, zinc, chromium, and cadmium were determined by atomic absorption spectrophotometry, employing standard procedures.[6] Mercury in selected effluents was determined by the FWQA Provisional Method for mercury (Flameless AA Procedure)[7] employing a Perkin Elmer Coleman Model 50 mercury analyzer system.

Selected effluents were also analyzed for total organic carbon, employing the Beckman Model 915 Total Carbon Analyzer,[6] and redox potentials of effluents from saturated columns were intermittently determined during the latter half of the studies by means of Orion Model 96-78 platinum redox electrodes. These electrodes were placed in effluent delivery tubes at points considerably removed from outlets to preclude possible interference resulting from back diffusion of atmospheric oxygen.

Control column effluents were subjected to all the analyses listed above except NTA Na_3 and ^{14}C.

Simulated Aquifer Studies

In order to investigate the possible degradation of NTA in an essentially anaerobic ground-water environment, model aquifers simulating as nearly

as possible conditions prevailing in a natural aquifer were constructed in the laboratory. Figure 3 shows details of the simulated aquifer design.

Each laboratory aquifer was constructed from a 4 l aspirator bottle containing 3 l of natural aquifer sand. A 6 mm O.D. borosilicate glass tube which extended through the rubber stopper sealing the aspirator bottle and into the aquifer sand almost to the bottom of the aquifer container served as a well shaft. This tube was perforated below the surface of the sand, with the perforations placed in a spiral arrangement. The tube was packed loosely with glass wool to prevent entry of aquifer sand into the water pumped from the aquifer and was topped with a 1/4 inch Swagelok Zytel tee which served as a well head. The side arm of this tee was connected to a closed loop of Tygon tubing which passed through a peristaltic pump and back to the aquifer unit where it was attached to a short piece of tubing which penetrated the sealing stopper. This system permitted water to be pumped from the saturated depths of the aquifer sand through the well head and returned via the closed tubing system to the aquifer unit. The upper arm of the well head tee was sealed with a Teflon-lined rubber septum through which the pumped stream could be sampled.

The stopper of each aquifer unit was also penetrated by a glass tee, one arm of which served as a port for evacuation and gassing of the simulated aquifer while the other arm was sealed by a rubber sleeve-type septum through which the gases above the sand and water could be sampled. In addition, each aquifer unit was provided with still another 6 mm O.D. tube penetrating to the gas space above the aquifer sand to serve as an outlet for pressure checks and venting of gases if needed.

Natural aquifer sand for construction of the simulated aquifers was obtained near Byars, Oklahoma, from a shallow aquifer underlying the floodplain of the South Canadian River. The sand was obtained by carefully excavating to a point slightly below the water table, then scooping the saturated sand into a sterile stainless steel bucket with a sterile scoop. The sand was then taken immediately to the laboratory and 3 l portions were loaded under aseptic conditions into each of three presterilized simulated aquifer units. After completion of sand loading one of these units was sterilized again at $121^{o}C$ for 30 minutes to provide a control.

Most of the water native to the aquifer sand was removed from all three units by applying a vacuum of approximately 29 inches of mercury at the bottom outlets of the aspirator bottles. Sterile solutions of NTA Na_3 in distilled water were then allowed to flow slowly into the evacuated units through the lower outlets until the liquid levels were approximately 25 mm above the sand levels. Approximately 700 ml of sterile NTA Na_3 solution were required for each simulated aquifer unit. The solution charged to all three aquifers contained 50 mg/l NTA Na_3. The feed solutions for the sterile control aquifer and one of the other units, designated Simulated Aquifer Number 2, contained 900 pCi/ml ^{14}C-NTA (uniformly labeled). The feed for the third aquifer unit, designated Simulated Aquifer Number 1, contained no isotopically labeled NTA. Initial concentrations of NTA Na_3 and ^{14}C in the aqueous

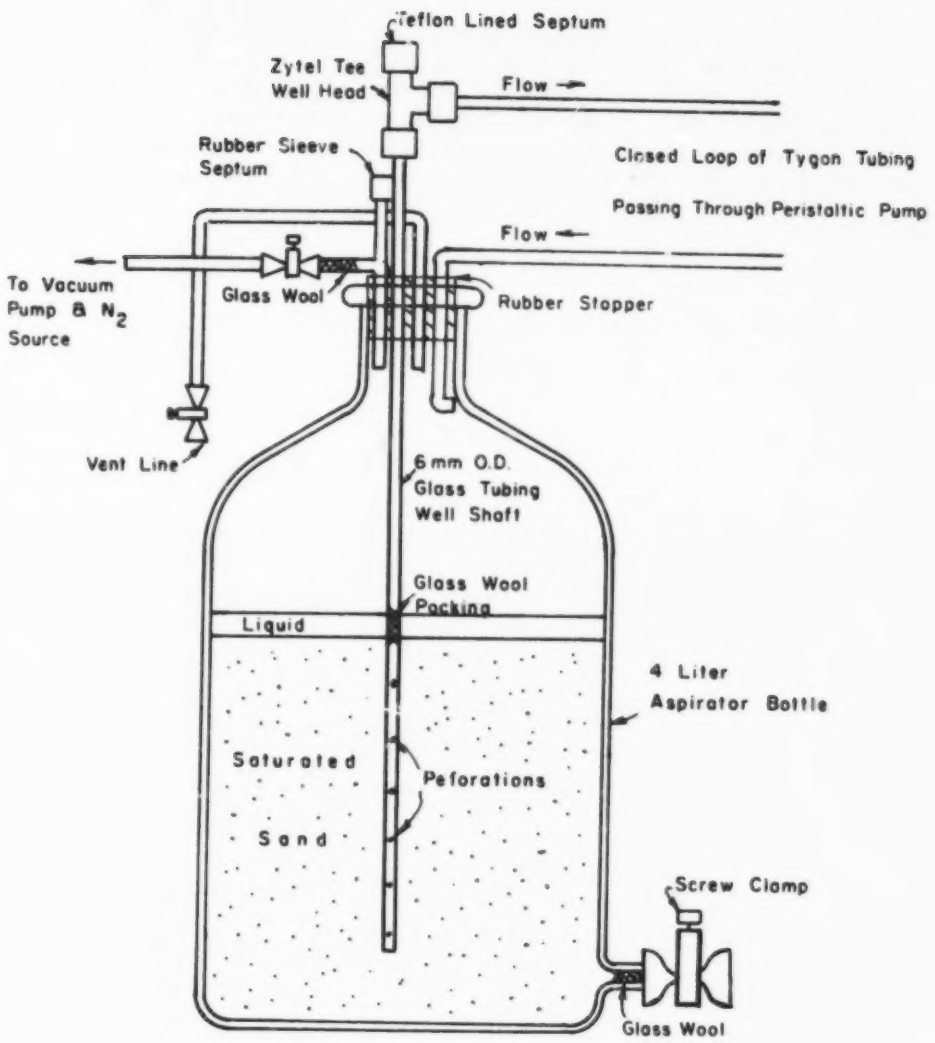

FIGURE 3. DETAILS OF SIMULATED AQUIFER DESIGN

phases of the aquifers were actually only 60-70 percent of concentrations in the feed solutions because of sorption of NTA on the aquifer sand and dilution of the feed solutions by native water remaining in this sand.

After being charged with NTA Na_3 solution, the simulated aquifers were twice thoroughly vacuum evacuated and refilled with nitrogen gas through the top gas ports in order to establish conditions of very low oxygen tension within these units. The three aquifers were then placed in a constant temperature room where they were maintained in the dark at 20°C throughout the period of investigation. Figure 4 pictures the simulated aquifers and peristaltic pump as arranged during operation.

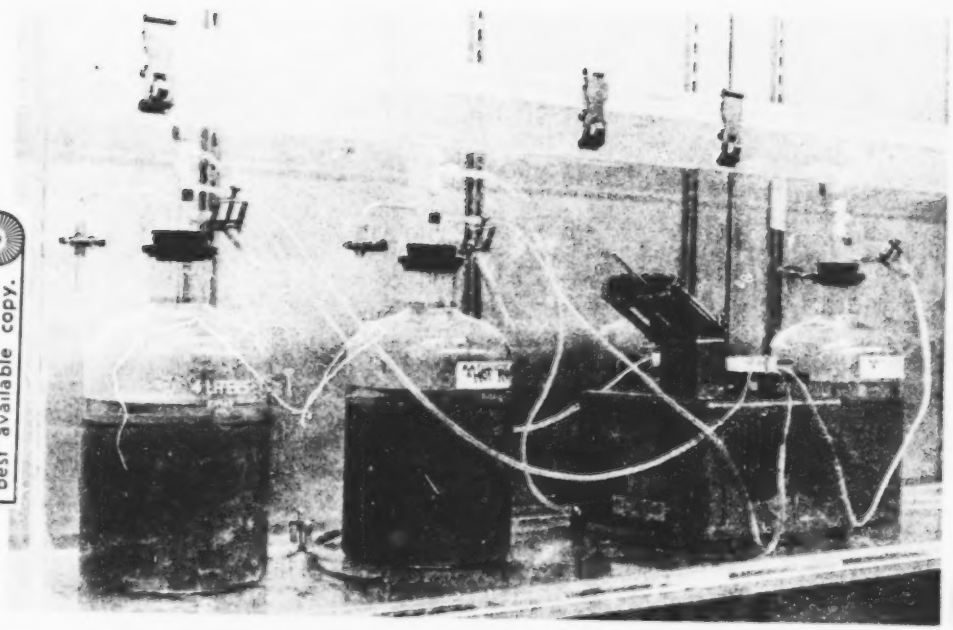

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FIGURE 4. SIMULATED AQUIFERS

The simulated aquifers were operated for a period of 265 days. They were recharged with solutions containing additional NTA after 52, 143, and 209 days of operation.

The first recharge was accomplished by aseptically injecting through the well head septums of both Aquifers Number 1 and 2 ten ml of sterile solution consisting of 60 mg of NTA Na_3 in distilled water. This solution was expected to increase NTA Na_3 concentrations in the water in the aquifers by 35-45 mg/l, but uncertainties regarding the actual volume of water in the aquifers and the quantity of NTA Na_3 that would be sorbed on aquifer sand precluded calculation of an exact quantity of NTA Na_3 needed to give a definite concentration in a recharged aquifer. The recharge solution for Aquifer Number 2 also included 13.2 µc of uniformly labeled ^{14}C-NTA which was expected to increase radioactivity 10-12 fold and hence facilitate radioautography studies. The control aquifer was not recharged at this time.

For the second recharge sterile solutions consisting of 60 mg of NTA Na_3 in 200 ml of distilled water were pipetted aseptically into Aquifers Number 1 and 2 through the gas sampling ports, after removal of the sleeve-type septums, in order to replenish both NTA and water levels in the units. A 200 ml solution containing 30 mg of NTA Na_3 was similarly added to the control aquifer. The recharge solutions for Aquifer Number 2 and the control also contained 39.6 µc each of ^{14}C-NTA. All septums and worn tubing were changed at this time, and the units were re-evacuated and re-gassed with nitrogen. Also, to further preclude the possibility of oxygen entering the aquifer units, all three units and the peristaltic pump system were at this time placed in a specially constructed plexiglass box filled with nitrogen and were maintained there for the remainder of the investigation (Figure 4).

The third recharging of Aquifers Number 1 and 2 was conducted by essentially the same procedure as that employed in the second recharging. However, the 200 ml of recharge solution also contained 0.5 ml Sego in order that the effect of an extraneous carbon source on NTA degradation in the aquifers might be observed. On the basis of the BOD of Sego, these solutions should have imparted a BOD in the range of 60-90 mg/l to the water in the aquifer. The control aquifer was recharged with 100 ml of sterile solution consisting of 0.5 ml Sego in distilled water with no NTA.

The aquifer units were pumped occasionally for a few hours to simulate movement of ground water and to maintain as much uniformity as possible within the units, particularly after recharging. Units were always pumped for a short period immediately before sampling in order to obtain representative samples from the depths of the aquifers. Sampling, which was generally conducted at 3-7 day intervals throughout these studies, was accomplished by withdrawing required quantities of liquid through the well head septums by means of sterile syringes while the units were being pumped.

Samples taken from the simulated aquifers were analyzed for NTA Na_3 by the automated zinc-zincon method and for ^{14}C by liquid scintillation spectrometry as previously described. Selected samples were also subjected to radioautography, employing essentially the same procedures as used for soil column effluents, except that 10-50 µl aliquots of aquifer water samples were usually chromatographed with no prior concentration. This chromatography of dilute samples was an effort to avoid chromatographic migration problems encountered in the soil column work resulting from concentration of salts and possibly other substances present in the samples. Use of the dilute samples for radioautography was possible because of the relatively high activity of the aquifer samples after the first recharge. Autograms were also exposed for as long as 96 days in an effort to detect substances present only in very low quantity on the chromatograms.

The composition of the gas above the water and sand in the simulated aquifer units was determined each time a liquid sample was obtained. A Varian-Aerograph 90 P gas chromatograph equipped with an internal and external column in series was employed for these analyses. The internal (first) column was 80/100 mesh Porapak Q (6.35 mm x 183 cm) operated at 55°C while the external (second) column was 60/80 mesh Molecular Sieve 5A (6.35 mm x 92 cm) operated at room termperature (23-25°C). Carrier gas (He) flow rate was 50 ml/min. This system permitted analyses for methane, carbon dioxide, oxygen, and nitrogen with a single injection of sample.

SECTION V

RESULTS AND DISCUSSION

Sorption Studies

The data obtained for sorption of NTA on Burleson clay loam, Claremore loam, and Konawa loamy fine sand soils in this investigation are best described by means of the Freundlich adsorption isotherm, as shown in Figure 5. Greatest sorption was evidenced by the loam soil, with the sand being least effective as a sorbant. At an equilibrium concentration of 50 mg/l of NTA Na_3 in water sorption values for the loam, sand, and clay-loam soils were 64, 28, 8.7 µg NTA Na_3 per gram of soil, respectively. Analogous data at 5 mg/l NTA Na_3 were 10.2 µg/g, 3.5 µg/g, and 0.98 µg/g.

These data show that NTA is not strongly sorbed by any of the three soils studied. The relatively weak sorptive forces exhibited by these soils toward NTA cannot, however, be completely discounted in considering the movement of NTA into and through ground water because of the high ratio of soil encountered by water infiltrating through the soil mantle and moving within the water table. This is illustrated by considering the movement of NTA through a hypothetical 10 ft^3 column of soil of 1 ft^2 cross sectional area and 10 ft depth.

Data obtained in column preparation for the soil column studies (see Table 1) indicate that a 10 ft^3 column of dry Claremore loam would weigh about 352 Kg and would hold approximately 126.5 l of water when saturated. The sorption data obtained in this work (y/m = 62 µg/g at C = 50 mg/l) (Figure 5) show that in order for the water in the column of loam to contain 50 mg NTA Na_3/l under equilibrium conditions there would necessarily be a total of about 22.5 g NTA Na_3 sorbed on the soil. Assuming plug flow and absence of non-equilibrium conditions, it can be calculated that in order for the NTA Na_3 concentration of the effluent from this column of soil to equal the influent concentration the column would have to be dosed for approximately 76 days at the daily rate of 2 gal/ft^2 if the influent concentration were 50 mg NTA Na_3/l. If there were no sorption of NTA by the soil, theoretically only 17 days of such dosing would be required for influent and effluent NTA concentrations to be identical. Hence, the time required for an NTA Na_3 solution of 50 mg/l to move through the Claremore loam would appear to be increased by 4-5 fold as the result of sorption of the NTA on the soil particles. Similar calculations indicate a 6-7 fold increase in migration time through the loam soil for a solution containing 5 mg NTA Na_3/l because of the relatively greater proportion of NTA sorbed at lower concentrations. For the Konawa loamy fine sand migration times for 5 to 50 mg/l solutions of NTA Na_3 are indicated by such calculations to be increased only about two-fold as the result of sorption effects.

These calculations, while admittedly crude, do indicate that under some circumstances sorption on soil particles could considerably retard the rate of infiltration of NTA into ground water and the movement of this compound

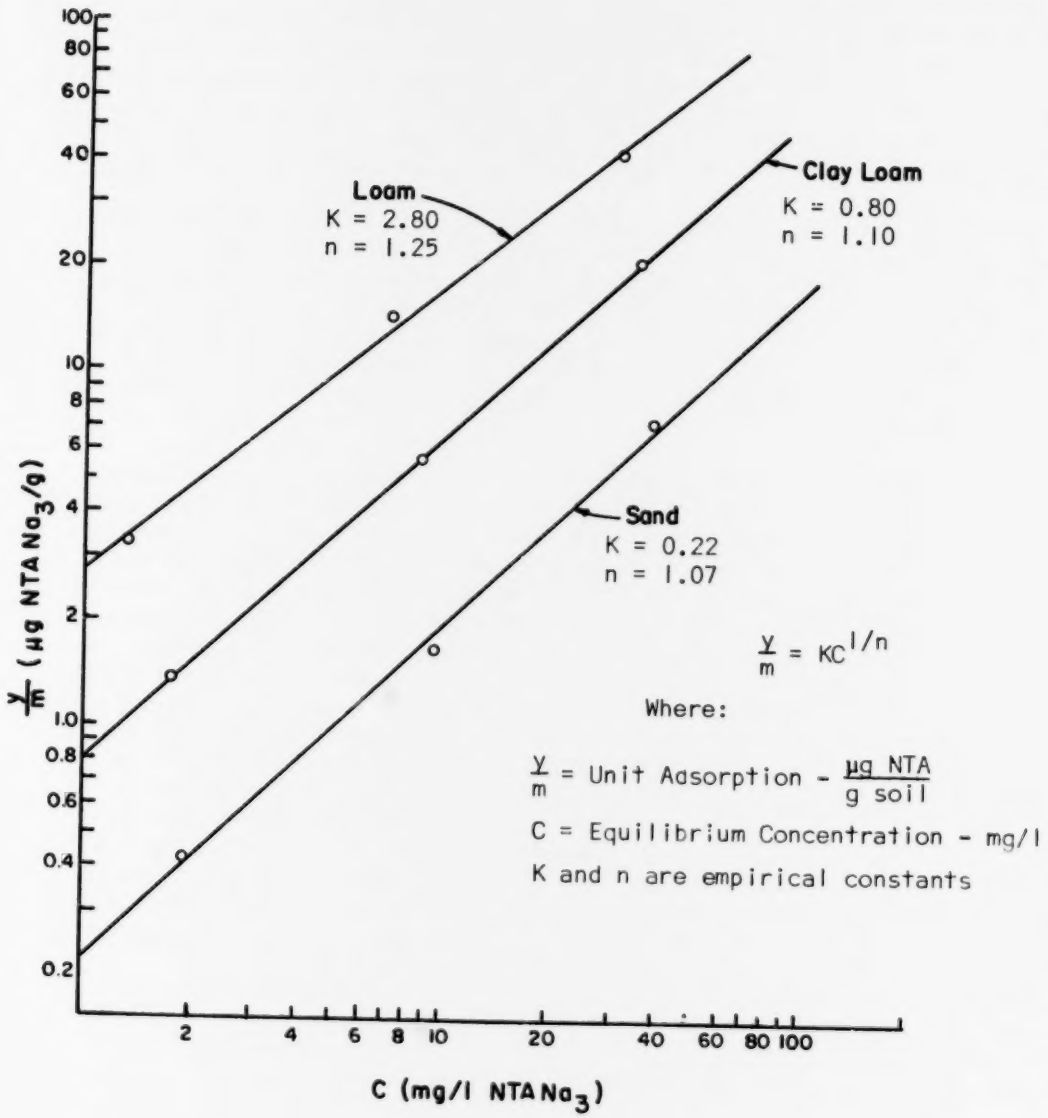


FIGURE 5. NTA SORPTION: FREUNDLICH ISOTHERM AT 20° C

within aquifers. Nevertheless, as an individual mechanism, sorption of NTA by soils does not appear to be sufficient to greatly reduce the potential pollution of ground waters by this compound over the course of its long-term usage as a detergent builder. However, by retarding the movement of NTA in soils and hence effectively increasing its residence time in regions of high microbial activity sorption may play a significant secondary role in the removal of NTA from infiltrating waters by microbial degradation.

Soil Column Studies

Studies Employing Natural Soils

The results obtained in the soil column experiments concerned with the effect of infiltration of NTA through unsaturated (aerobic) sand, loam, and clay-loam soils are reflected in Figures 6-8, which present graphically the concentrations of NTA, radioactive carbon, and selected metals occurring in the unsaturated soil column effluents during the 77-day period of investigation.

As shown in Figure 6, NTA was present in the effluent from the unsaturated sand column from the second through the ninth day of operation, with a peak level near feed concentration occurring on the fifth day. By the tenth day, however, NTA had virtually disappeared from this effluent and was not again detected as an effluent constituent during the remaining 67 days of operation. Essentially no NTA appeared in effluents from the unsaturated loam and clay loam columns at any time during the 77 days of operation, even though approximately 29 mg of NTA Na_3 were applied daily to each column (Figures 7 and 8). The early presence and subsequent disappearance of NTA in the sand column effluent undoubtedly reflected a short acclimation period required for establishment within the soil of a microbial population capable of degrading NTA. Because of the greater sorptive power of the loam and clay-loam soils, the movement of NTA in these columns was probably retarded sufficiently that acclimation and subsequent degradation occurred before any NTA traversed the lengths of these columns.

During most of the period of operation, effluents from all three unsaturated soil columns contained significant quantities of ^{14}C which were not accountable as NTA, thus indicating the presence in these effluents of products of NTA degradation. Thin-layer chromatography and radioautography studies of selected effluent samples collected throughout the operating period did not reveal the presence of any organic degradation products of NTA in these effluents. Analysis of selected effluent samples from the three columns for $^{14}CO_2$ indicated that virtually all of the ^{14}C present in these effluents was incorporated in CO_2 except that appearing in ^{14}C-NTA in the early effluent samples from the sand column.

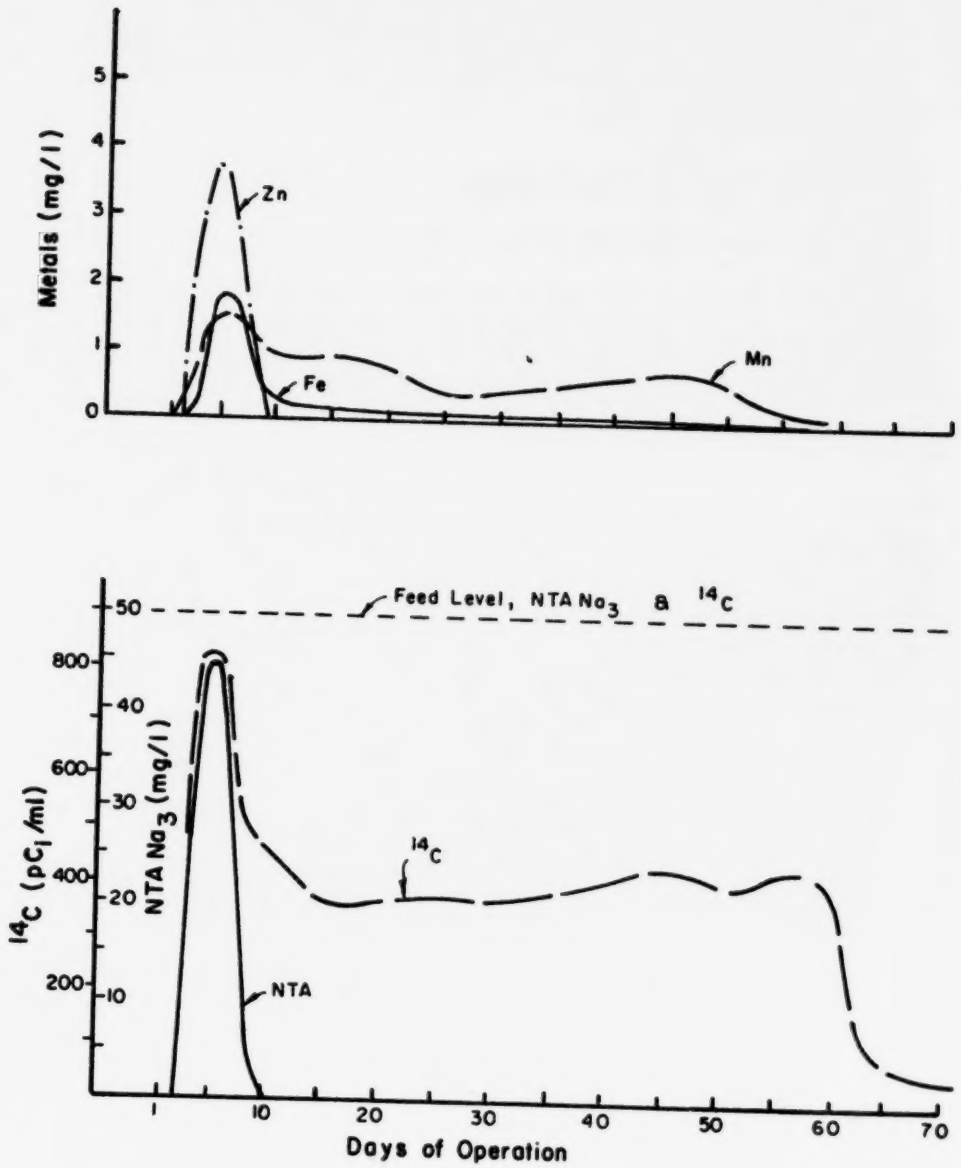


FIGURE 6. NTA, ^{14}C, AND METALS IN EFFLUENT FROM UNSATURATED SAND COLUMN

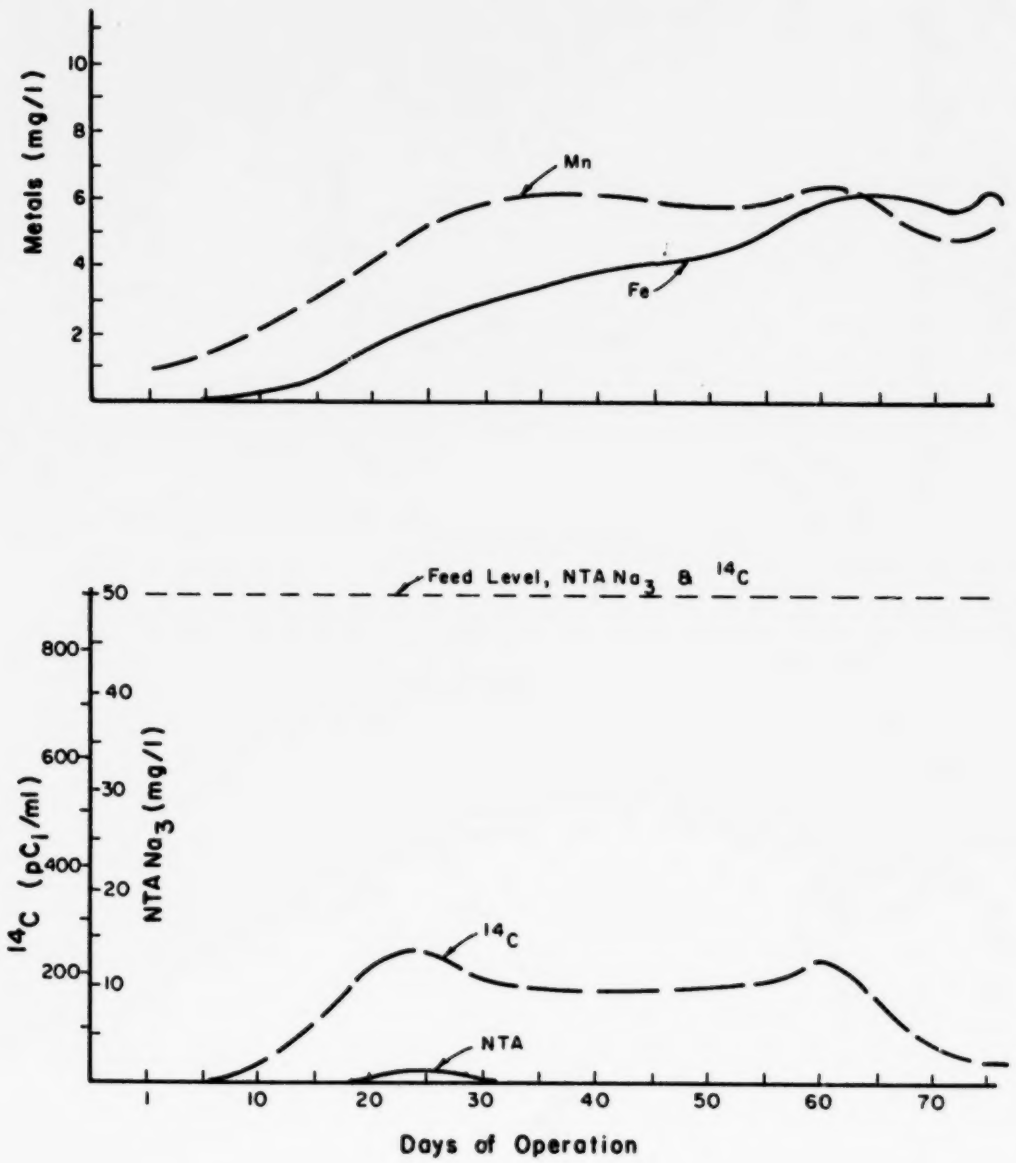


FIGURE 7. NTA, ^{14}C, AND METALS IN EFFLUENT FROM UNSATURATED LOAM COLUMN

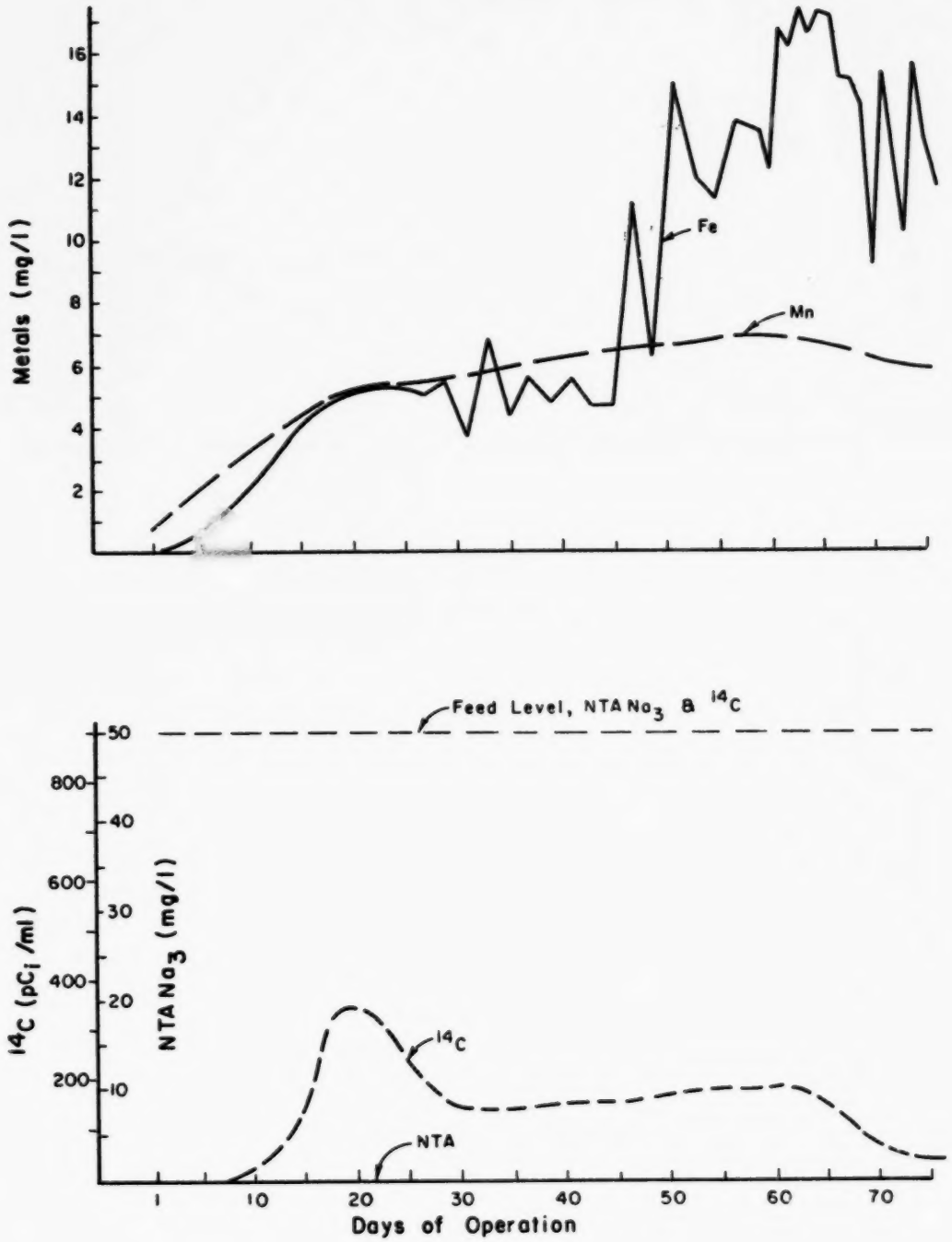


FIGURE 8. NTA, ^{14}C, AND METALS IN EFFLUENT FROM UNSATURATED CLAY LOAM COLUMN

As Figures 6, 7, and 8 show, a major portion of the radioactive carbon applied to the unsaturated soil columns never appeared in the column effluents. It seems likely that most of this ^{14}C was lost to the atmosphere as $^{14}CO_2$, with perhaps a small quantity being incorporated into cellular material in the columns. This is consistent both with the analytical data for the column effluents and the report by Thompson and Duthie which shows that aerobic microorganisms can degrade NTA completely to CO_2 and nitrate.(2)

These experiments with unsaturated soil columns indicate that NTA infiltrating through unsaturated soil systems probably will undergo rapid and complete degradation, with the only products likely to enter ground waters as a result of such degradation being CO_2 and probably inorganic nitrogen compounds. The magnitude of additional inorganic nitrogen pollution of ground water which is likely to result from the projected use of NTA in detergents is probably not sufficient for critical concern. For example, complete degradation in unflooded septic tank percolation fields of 35 mg NTA Na_3/1, a concentration which could occur in septic tank effluents if detergents containing 25 percent NTA Na_3 were used,(8) would result in a maximum increase of only 1.91 mg of nitrogen in each liter of percolate entering underlying ground waters. Nevertheless, introduction into ground waters of additional nitrogen in the quantities likely to result from NTA usage in detergents is certainly less than desirable, and could result in problems in aquifers where wide fluctuations of water tables may result in salt concentration through sequential deposition and resolubilization.

Concentrations of zinc and iron in the effluent from the unsaturated sand column attained peak levels when NTA was present in highest concentration in this effluent and declined significantly when NTA disappeared from the effluent (Figure 6). Hence, NTA would appear to be implicated in the leaching of these metals from the soil. Manganese concentrations also peaked in conjunction with NTA concentration, but remained relatively high after NTA had disappeared from the effluent.

Relatively high concentrations of manganese and iron appeared in the effluents from the unsaturated loam and clay-loam soil columns as dosing of the columns with NTA progressed (Figures 7 and 8). In the absence of control columns not dosed with NTA, however, it cannot be ascertained if leaching of these soils metals was in any way related to infiltration of NTA into the soil. The fact that iron and manganese concentrations in the effluents did not decline significantly when NTA dosing of the columns was terminated casts doubt on existence of such a relationship. The possibility was not eliminated, however, that increased quantities of metals might enter ground waters as a result of a mechanism involving initial solubilization of soil metals through formation of NTA chelates, with the metals remaining in solution and continuing to move through the soil after degradation of the NTA.

Figures 9, 10, and 11 show graphically the concentrations of NTA Na_3, ^{14}C, and metals appearing in the effluents from the saturated sand, loam, and clay-loam soil columns during the initial experiments concerning the effect of infiltration of NTA through saturated (anaerobic) soils systems.

As shown by these figures, NTA first appeared in column effluents on the fourth, eleventh, and seventh day of operation respectively for the sand, loam, and clay-loam columns. NTA Na_3 in the saturated sand column effluent attained peak concentrations of about 46 mg/l during the period of the ninth through eleventh days of operation, with ^{14}C showing a corresponding peak of about 935 pCi/ml, which was somewhat above the ^{14}C feed level of 900 pCi/ml (Figure 9). In the saturated loam column effluent a peak NTA Na_3 concentration of nearly 59 mg/l, which was considerably above the feed level of 50 mg/l, and a corresponding ^{14}C peak in the neighborhood of 1160 pCi/ml were exhibited on the sixteenth day of operation (Figure 10). After attaining these peaks, concentrations of NTA Na_3 in effluents from both the saturated sand and loam columns decreased and remained within the range of 65-85 percent of feed levels until dosing of the columns with NTA Na_3 was terminated. Following the initial peaks, ^{14}C levels in both effluents also decreased and were generally 80-95 percent of feed concentration for the remainder of the dosing period.

The effect of dosing NTA Na_3 to the saturated clay-loam column was quite different than the effect of similar operation of the sand and loam columns during the first 30 days of study. As Figure 11 indicates, both NTA Na_3 and ^{14}C effluent concentrations attained relatively low peaks on the 14th day of operation and then declined to minima on about the 29th day. The decline in NTA Na_3 and ^{14}C concentrations from the 14th to 29th days of operation was attributed to aerobic degradation of NTA resulting from the presence of air in the capillary fringe of the column and the entrapment of air pockets in the soil interstices throughout the column. After about the 30th day of operation, the saturated clay-loam column began performing in a manner similar to the other saturated columns, probably at least partially as a result of intentional flooding of the capillary fringe of the column on the 29th day. Depletion of oxygen in trapped intersticial pockets of air, leading to a more truly saturated state within the column, was also probably significantly involved in this change in column performance.

There appears to be no ready explanation for the peak concentrations exceeding feed levels of ^{14}C in effluents from the saturated sand and loam columns and of NTA Na_3 in the effluent from the loam column. However, the fact that both NTA Na_3 and ^{14}C effluent concentrations were less than feed levels and that ^{14}C effluent levels were equivalent to 2-10 mg/l more NTA Na_3 than actually appeared in column effluents during most of the operating period for both the saturated sand and loam columns and for the clay-loam column after the 30th day, indicate that some degradation of NTA was occurring within these columns. Analysis of column effluents for $^{14}CO_2$ revealed that a major portion of the ^{14}C present in form other than NTA was incorporated in CO_2. However, thin-layer chromatography and radioautography of selected effluent samples obtained throughout the study showed clearly that some of this ^{14}C was present as a component of at least one organic degradation product of NTA.

Unknown substances in the effluent samples which caused migration anomalies on thin-layer chromatograms permitted thin-layer chromatographic analysis of the effluents only by means of the system employing Amberlite CG-400

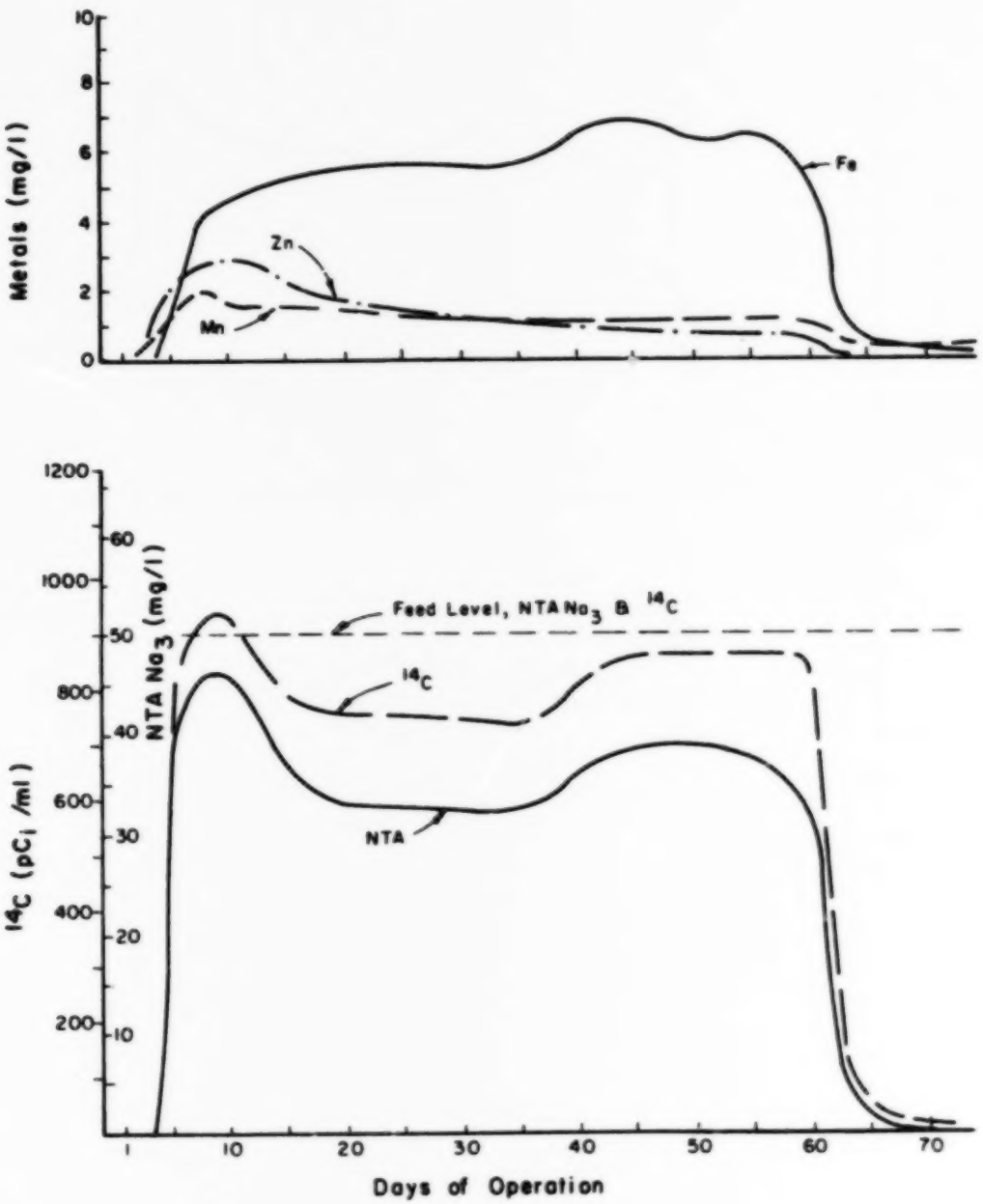


FIGURE 9. NTA, ^{14}C, AND METALS IN EFFLUENT FROM SATURATED SAND COLUMN

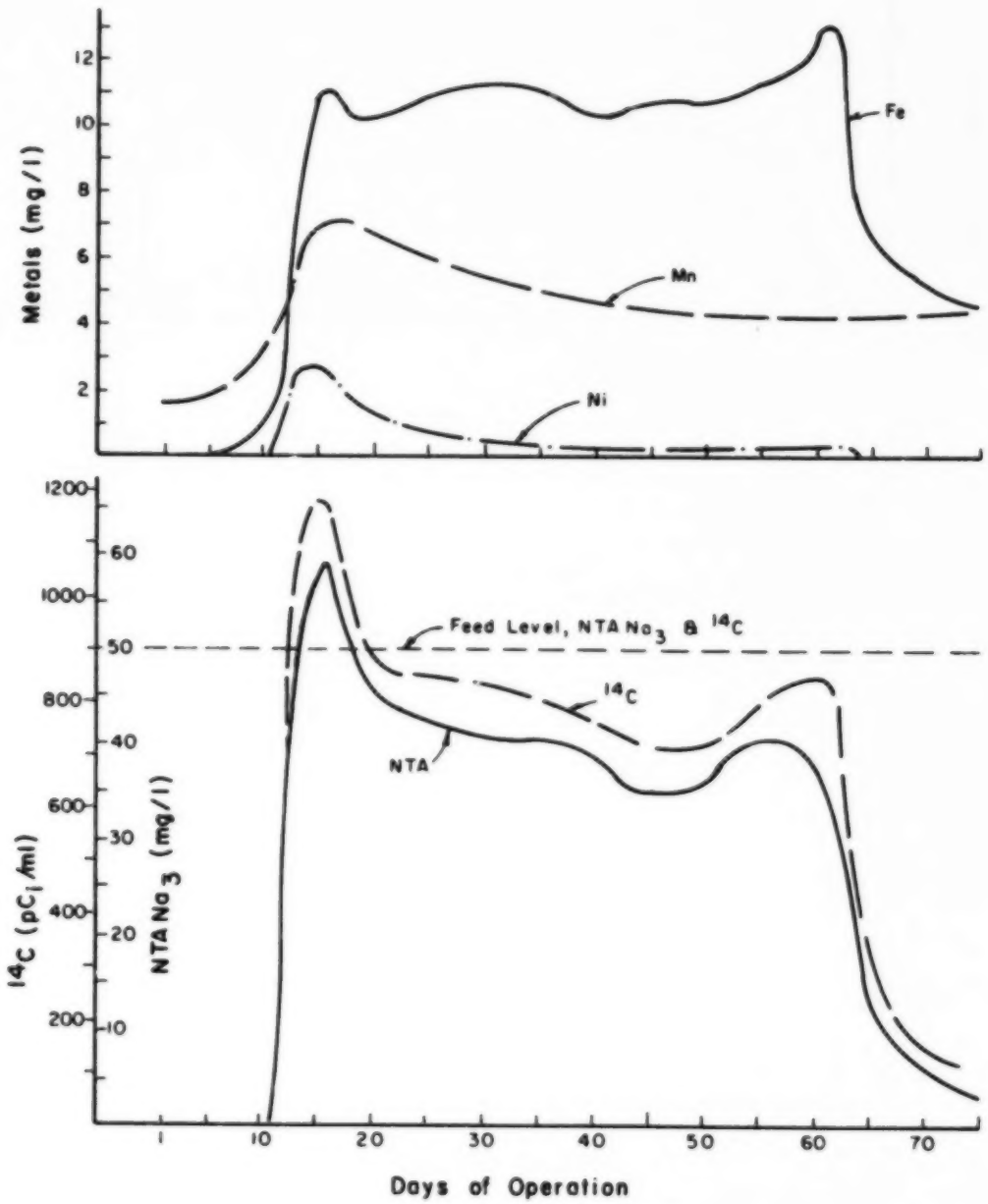


FIGURE 10. NTA, ^{14}C, AND METALS IN EFFLUENT FROM SATURATED LOAM COLUMN

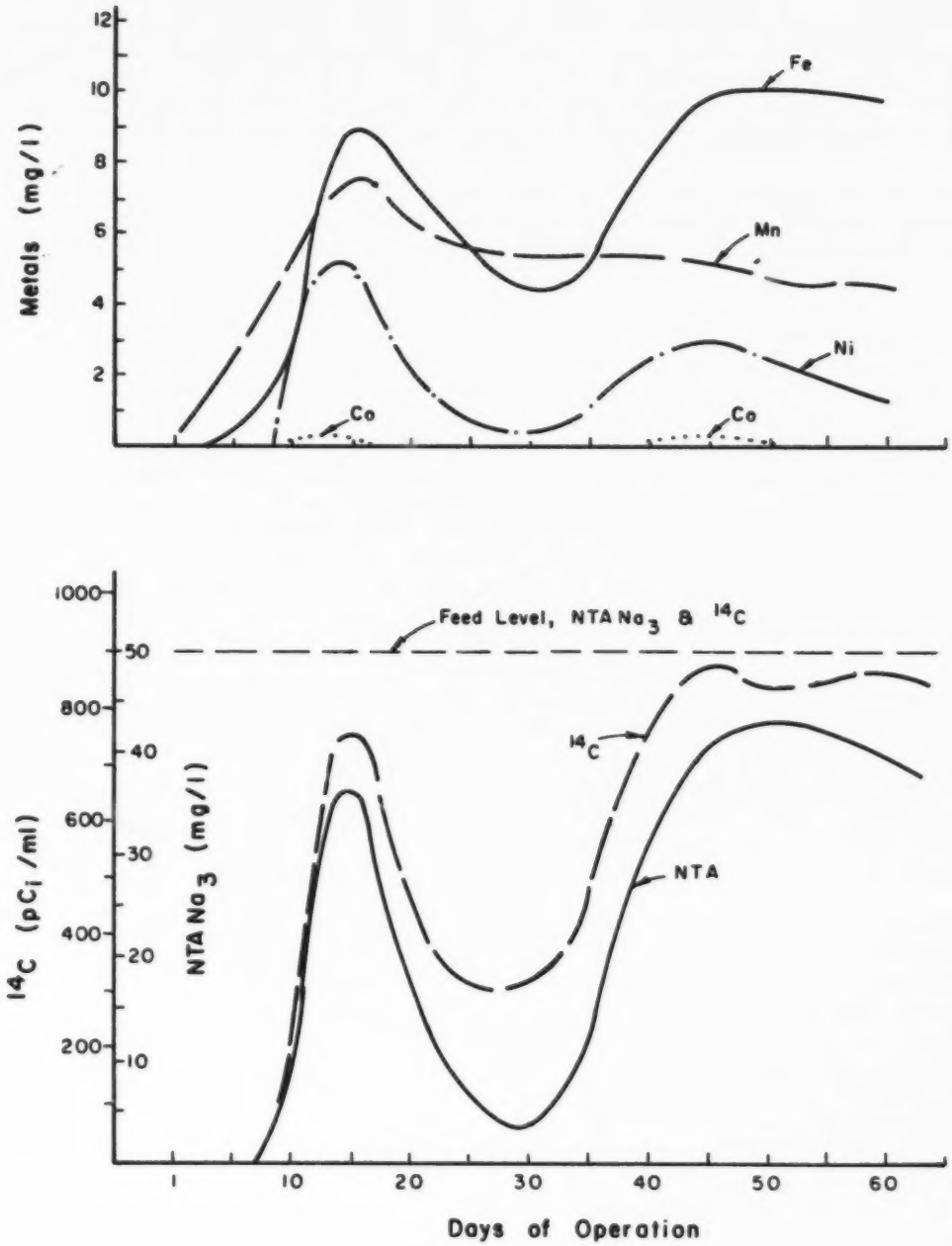


FIGURE 11. NTA, ^{14}C, AND METALS IN EFFLUENT FROM SATURATED CLAY LOAM COLUMN

resin-Avicel SF as stationary phase with 0.15 N NaCl as mobile phase. In this system the corrected R_f value of the NTA degradation product occurring in the saturated column effluents appeared to most nearly correspond with that for iminodiacetic acid (see Table 2, page 13). However, iminodiacetic acid and several of the other postulated NTA degradation products have very similar R_f values in the CG-400 resin-Avicel SF-0.15 N NaCl system, and hence their differentiation is questionable when migrational problems such as those occurring in chromatography of the effluent samples are encountered.

The quantities of organic product of NTA degradation present in the saturated soil column effluents were apparently quite low, and further efforts to characterize this substance were not undertaken during these studies.

It cannot be ascertained conclusively from these experiments that the observed NTA degradation was truly anaerobic in nature, or if it was actually aerobic degradation which occurred in the capillary fringe regions of the columns and which was arrested by lack of oxygen as the feed solution percolated deeper into the columns. The possibility of aerobic degradation is supported by the following facts: feed solutions contained some oxygen when they entered the tops of the soil columns because of the dosing procedure employed; and, intentional flooding of the capillary fringe of the saturated sand column on the 35th day of operation resulted in a decrease in the amount of NTA degradation occurring in this column (Figure 9). However, more than twenty percent of the NTA Na_3 entering the saturated sand column was apparently degraded even after flooding of the capillary fringe. This observation, combined with confirmed anaerobic degradation of NTA in simulated aquifer studies described later in this report, provides support for the occurrence of at least some true anaerobic degradation of NTA in the saturated soil columns. Initial limited aerobic degradation followed by slow anaerobic decomposition would appear a distinct possibility. The possibility of such a sequence gives reason to speculate that the organic degradation product of NTA observed in these studies might have resulted from arrested aerobic degradation.

Overall, these studies with saturated sand, loam, and clay-loam soil columns indicate that NTA infiltrating through saturated soil systems, such as flooded septic tank percolation fields or under waste water lagoons, will likely undergo at most only slow degradation, and hence high proportions will probably reach ground water essentially unchanged. The possibility is suggested that NTA degradation products of possible health concern[9] might be produced in saturated soils, but the evidence for this possibility is tenuous and if such compounds should indeed be produced, the quantities entering ground water would likely be extremely small.

As indicated in Figures 9, 10, and 11, there were generally good correlations between concentrations of certain metals and concentrations of NTA Na_3 in effluents from the three saturated soil columns. These metals were: iron, zinc, and manganese for the sand column; iron and nickel for the loam column; and, iron, nickel, and cobalt (although the concentration of the latter element was never very high) for the clay-loam column. The decreases in metals concentrations in the sand and loam column effluents which accompanied decrease in NTA Na_3 concentrations following termination of NTA Na_3 dosing on the 58th day of operation appear particularly significant. Observation of the effects of termination of NTA dosing on metals concentrations in the effluent from the saturated clay-loam column was not possible because clogging and resulting poor flow performance precluded the collection of further meaningful data from this column after about the 60th day. However, the minima in effluent metals concentrations corresponding to the minimum in NTA Na_3 concentration occurring on the 29th day of operation provides significant additional information concerning the effect of infiltrating NTA on the metals in the clay-loam soil.

Reasonable caution must be exercised in interpreting the metals data obtained in these experiments with saturated natural soils because of the absence of data from control columns. Nevertheless, the studies do appear to indicate strongly that NTA solutions infiltrating through saturated soil systems are likely to solubilize and transport into ground water some metals native to the soils.

Studies Employing Sand Enriched with Metals

In Figures 12 and 13 are presented results obtained when solutions containing ^{14}C labeled NTA Na_3 were infiltrated through both unsaturated and saturated columns of Konawa loamy fine sand enriched with metals sludge containing lead, cadmium, chromium, zinc, and mercury.

As Figure 12 shows, NTA first appeared in the effluent from the unsaturated column on the 19th day of operation and attained a maximum concentration of 49 mg NTA Na_3/l (73 percent of the 67 mg NTA Na_3/l feed) on the 39th day. Thereafter, NTA concentrations declined slowly and became relatively stable at about 25 percent of feed level after the 70th day. Radioactive carbon levels generally were very close to equivalent NTA Na_3 concentrations during the first 54 days of operation, but then remained at higher levels (40-55 percent of feed) than NTA for the remaining period of study.

Cadmium levels in the effluent from this column correlated well with NTA Na_3, reaching peak concentrations of about 14 mg/l at 40-44 days of operation. Iron, which was not added in the metals sludge, first appeared in the effluent on the 4th day of operation and ranged between 2 and 3 mg/l from the 17th day to the 55th day, while very low levels (maximum about 0.5 mg/l)

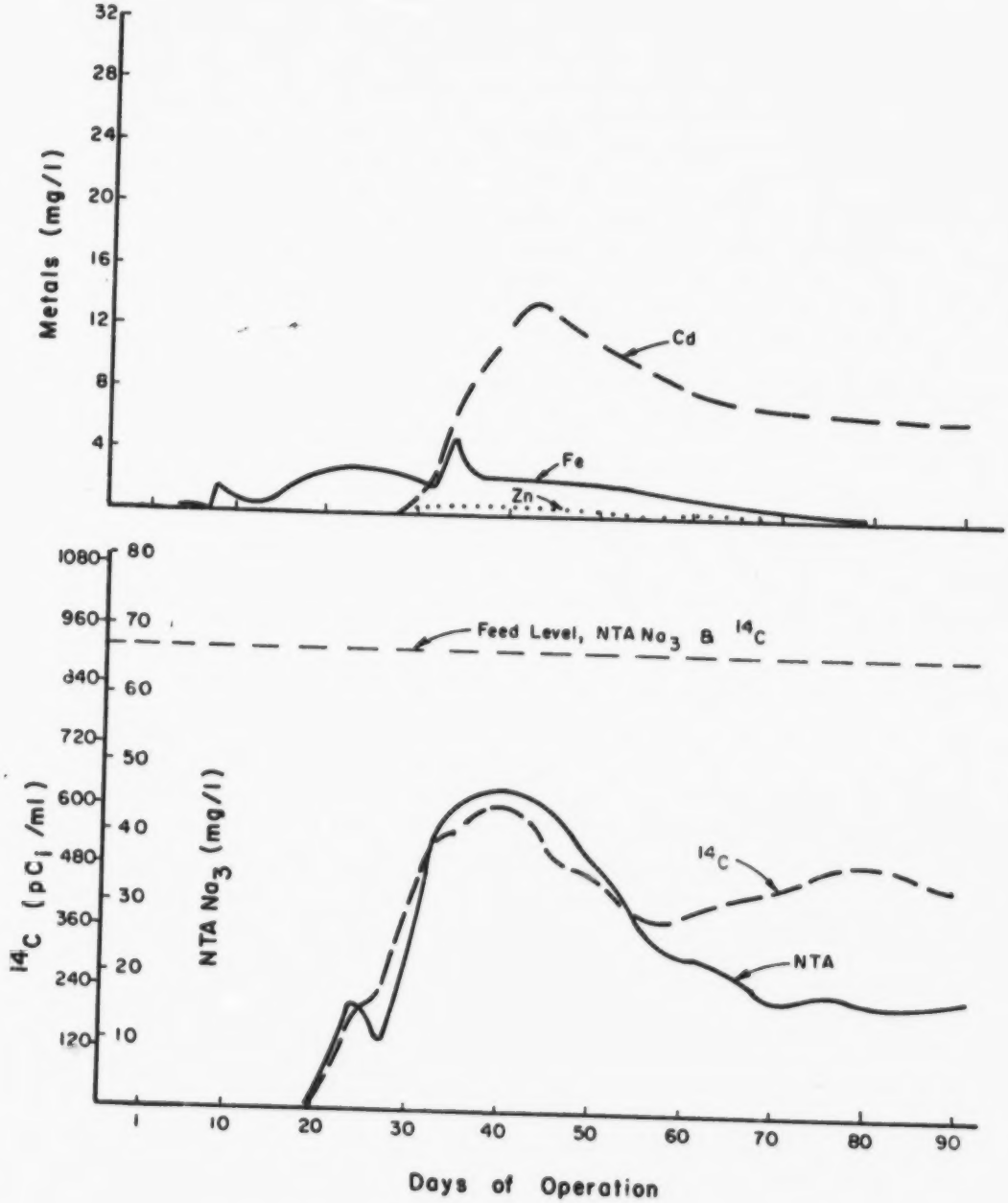


FIGURE 12. NTA, ^{14}C, AND METALS IN EFFLUENT FROM UNSATURATED SAND-METALS SLUDGE COLUMN

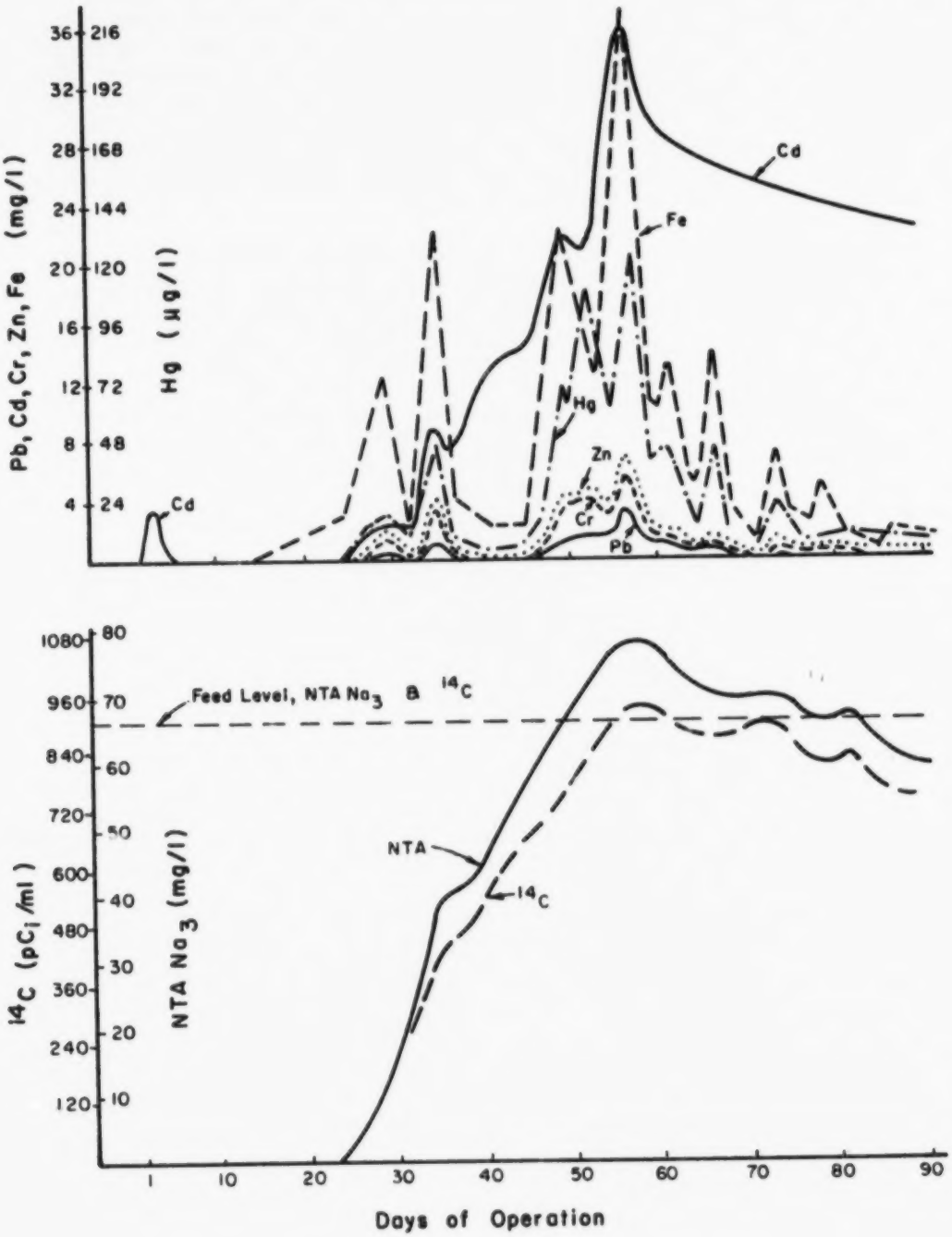


FIGURE 13. NTA, ^{14}C, AND METALS IN EFFLUENT FROM SATURATED SAND-METALS SLUDGE COLUMN

of zinc were present in the effluent when maximum concentrations of NTA occurred. The effluent from the control column of sand enriched with metals sludge, which was dosed only with water or water and Sego, contained some cadmium during the first 4 days of operation but none thereafter. The quantity of cadmium eluted from the experimental column dosed with NTA was at least ten-fold greater than that eluted from the control column. The control effluent contained only very low levels of iron (maximum 0.3 mg/1) from the 27th day through the 53rd day and did not contain zinc at detectable levels (0.05 mg/1) at any time during the study.

Figure 13 shows that NTA first appeared in the effluent from the saturated column of sand enriched with metals sludge on the 22nd day, attained a maximum concentration of about 80 mg NTA Na_3/1 (119 percent of the 67 mg/1 feed level) on the 57th day, and then slowly declined to about 60 mg NTA Na_3/1 at termination of the experiment. Radioactive carbon effluent levels paralleled NTA Na_3 concentrations throughout the period of operation, but during much of this period were equivalent to as much as 15 percent less NTA Na_3 than indicated to be present in the effluent by the zinc-zincon analytical method. This discrepancy may have resulted from presence in the effluent of some unknown substance causing a positive error in the zinc-zincon analytical procedure. Limited studies involving purification of NTA in effluents by thin-layer chromatography followed by analysis by the zinc-zincon method gave some credence to this postulate. Color in some of the samples may have produced a quenching effect, contributing to some reduction in apparent ^{14}C levels also, although experimental evaluation of this possibility indicated that any such quenching which occurred was very limited in effect. At any rate, the NTA Na_3 and ^{14}C analytical data obtained appeared adequate to suffice for the purposes of this study.

Cadmium levels in the effluent from the saturated sand-metals sludge column generally correlated well with NTA Na_3 concentrations, attaining a maximum of about 36 mg/1 on the 56th day of operation when the NTA Na_3 concentration also was highest. Iron also appeared in the effluent at a maximum concentration of 38 mg/1 coinciding in time with the peak NTA Na_3 level. However, iron concentrations were erratic, showing several peaks and valleys. Considerably less total iron than total cadmium was eluted from the column over the period of operation. In addition, lesser quantities of zinc, chromium, lead, and mercury appeared in the effluent during the period that NTA was present, with peak concentrations generally appearing in synchrony with iron peaks. Maximum observed concentrations for these metals were: Zn, 7.1 mg/1; Cr, 5.8 mg/1; Pb, 3.8 mg/1; Hg, 122 µg/1. The effluent from the control column of saturated sand enriched with metals sludge contained relatively very low levels of cadmium (maximum 5 mg/1), mercury (maximum 2 µg/1), and iron (maximum 2 mg/1) on a few isolated occasions during the study. For the most part, however, levels of the metals determined in the control effluent were below detectable limits (less than: 0.05 mg/1 for Fe, Zn, and Cd; 0.2 mg/1 for Cr; 0.3 mg/1 for Pb; and 0.05 µg/1 for Hg) during the study.

Results obtained when NTA was infiltrated through a saturated column of Konawa loamy fine sand enriched with ores of lead, cadmium, chromium, zinc,

and mercury are presented graphically in Figure 14. As this figure shows, NTA Na_3 first appeared in the effluent from this column on the third day of operation, attained a concentration near the feed level (67 mg/l) on the seventh day, and remained near feed level throughout the remaining 85 days of the study. Radioactive carbon levels in the effluent followed NTA Na_3 concentrations very closely except during the period of the 5th through about the 20th day of operation when, as in the case of the saturated sand-metals sludge column, ^{14}C levels were significantly below equivalent NTA Na_3 concentrations.

Iron was present in some concentration in the effluent from the saturated sand-ore column from the seventh day of operation to the end of the study. As with the saturated sand-metals sludge column these effluent concentrations of iron were erratic, showing major peaks of about 13 mg/l and 37 mg/l on the 32nd and 45th day of operation, respectively. Zinc first appeared in the effluent on the third day of operation, attained a peak concentration of 3.2 mg/l on the 9th day, and was present at concentrations below 0.5 mg/l from the 20th day until termination of operation except for low peaks occurring when maximum iron concentrations were noted. Low concentrations of chromium (maximum 2.1 mg/l), cadmium (maximum 0.5 mg/l), lead (0.4 mg/l), and mercury (maximum 65 µg/l) also appeared in the effluent when maximum iron concentrations were present. Concentrations of these metals in the effluent from the control sand-ore column were generally below detectable limits. A low concentration of iron, peaking at 4.2 mg/l and exceeding 0.2 mg/l only during the 33rd through 45th day of operation, and several concentrations of mercury not exceeding 4 µg/l occurring from the 29th through the 36th day, were the only exceptions. The total quantities of these metals eluted from the control column were many times less than the total quantities eluted from the experimental column.

Comparison of the NTA and ^{14}C data obtained in this second series of soil column studies with similar data obtained from the unsaturated and saturated sand columns in the initial soil column studies (Figures 6 and 9) reveals that under both unsaturated and saturated conditions the movement of NTA through sand enriched with metals sludge (Figures 12 and 13) was very much slower than through sand alone. On the other hand, movement of NTA through saturated sand enriched with metal ores (Figure 14) was little different than movement of this compound through sand alone (Figure 9). Obviously the metal hydroxides that principally constituted the metals sludge exerted some retarding effect on infiltrating NTA not manifested by the metal ores, which were mostly sulfides. The mechanism of this retarding effect, however, remains a matter of conjecture.

Comparison of Figures 6 and 12 shows that although NTA infiltrating through the unsaturated sand column was completely degraded after a short acclimation period, a maximum of only about 75 percent degradation was achieved in the column containing sand enriched with metals sludge operated under similar conditions. It seems most likely that this effect was due to toxic effects of the heavy metals in the sludge which resulted in partial inhibition of

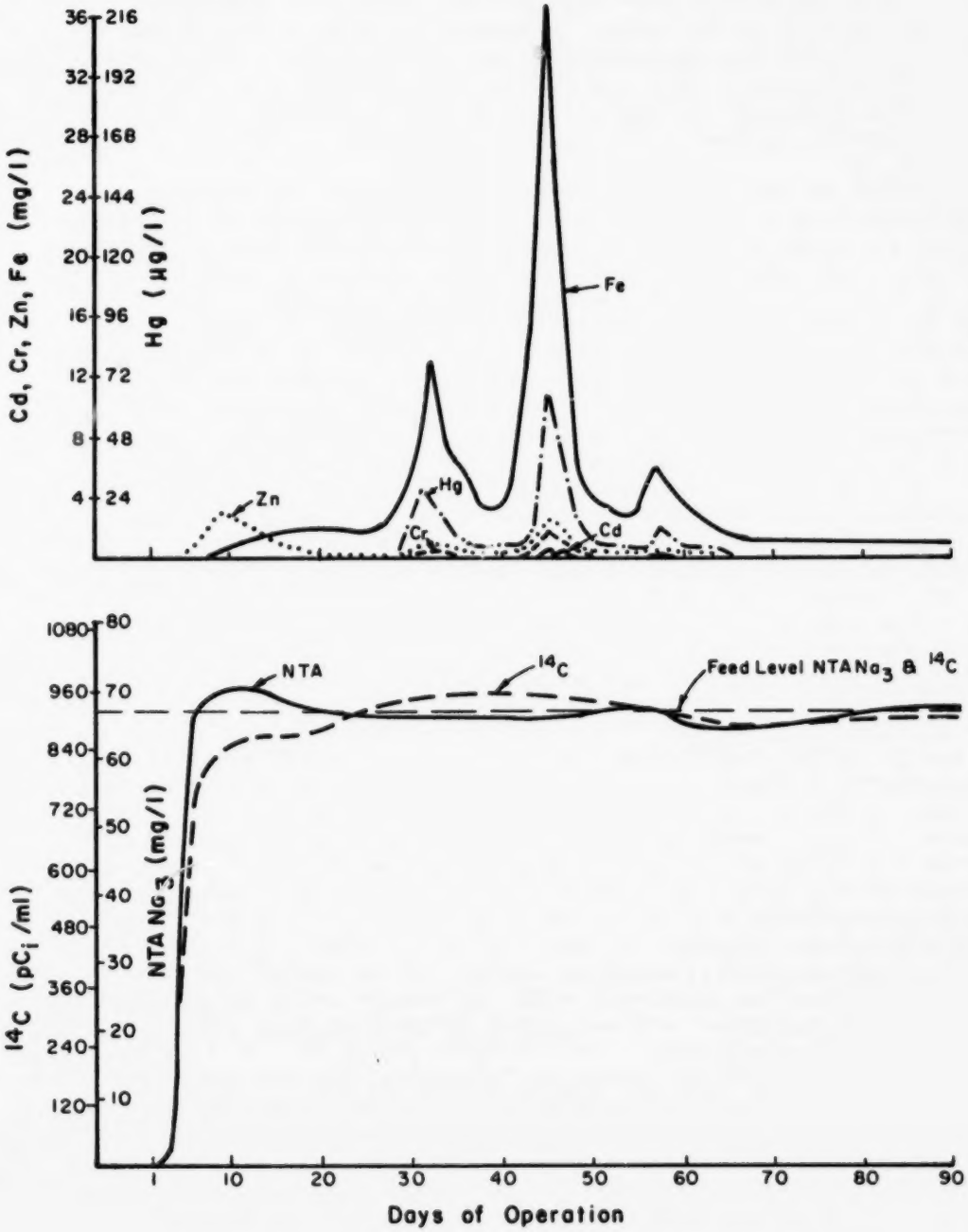


FIGURE 14. NTA, ^{14}C, AND METALS IN EFFLUENT FROM SAND-METAL ORES COLUMN

microbial activity in the column. Comparison of Figures 13 and 14 with Figure 9 reveals that if any degradation of NTA occurred in the saturated sand-metals sludge and sand-metal ores columns, it was certainly significantly less than occurred in the saturated sand column during the initial soil column studies. This also suggests the possibility of inhibition of NTA degradation due to metals toxicity, although more effective exclusion of oxygen from the upper zones of the saturated columns in the second series of soil column studies may have contributed to this apparently decreased degradation.

The presence of NTA appears to be the only explanation for the significantly greater metals concentrations in the effluents from the experimental columns than in the effluents from the control columns. The experimental and control column pairs were prepared from identical quantities of the same enriched soils and were operated by identical procedures except for the addition of NTA to the feed for the experimental columns. The pH values, which ranged between 7 and 8 for all the columns during most of the period of operation, were practically identical for the individual experimental and control column pairs. For the individual pairs of saturated columns there were essentially no differences noted in redox potentials of effluents from experimental and control columns. E_h values were determined only during the last half of the experimental period on an intermittent basis, but were found to vary very little, ranging near -400 mv for the saturated sand-metals sludge columns and -500 mv for the saturated sand-metal ores columns.

Differences in total organic carbon concentrations of effluents from experimental and control columns appeared to mainly reflect the presence of NTA in the experimental column effluent, as illustrated by Figure 15. The effect on TOC of adding sufficient Sego to impart a BOD of about 50 mg/l to feeds for both experimental and control columns is obvious in Figure 15. However, this additional carbon source in feeds produced no discernable effect on metals elution or NTA degradation in any of the columns under study.

There is no ready explanation for the "surges" of metals, particularly iron, occurring in the effluents from the saturated sand-metals sludge and sand-metal ores columns. It should be noted, however, that these effluents, which were generally somewhat more cloudy than control effluents, became extremely turbid and highly colored during periods of maximum metal elution This is illustrated by Figure 16, which pictures effluents from saturated sand-metals sludge experimental and control columns.

These experiments with sand columns enriched with selected metals leave little doubt that infiltration of water containing NTA through saturated soils containing heavy metals could result in solubilization and subsequent transport of such metals into ground waters. The extent and nature of such solubilization and transport in a specific situation will be dependent on a number of variables. This is illustrated by the qualitative and quantitative differences in the metals eluted from the sand-metals sludge and sand-metal ores columns in these studies. These variables will undoubtedly

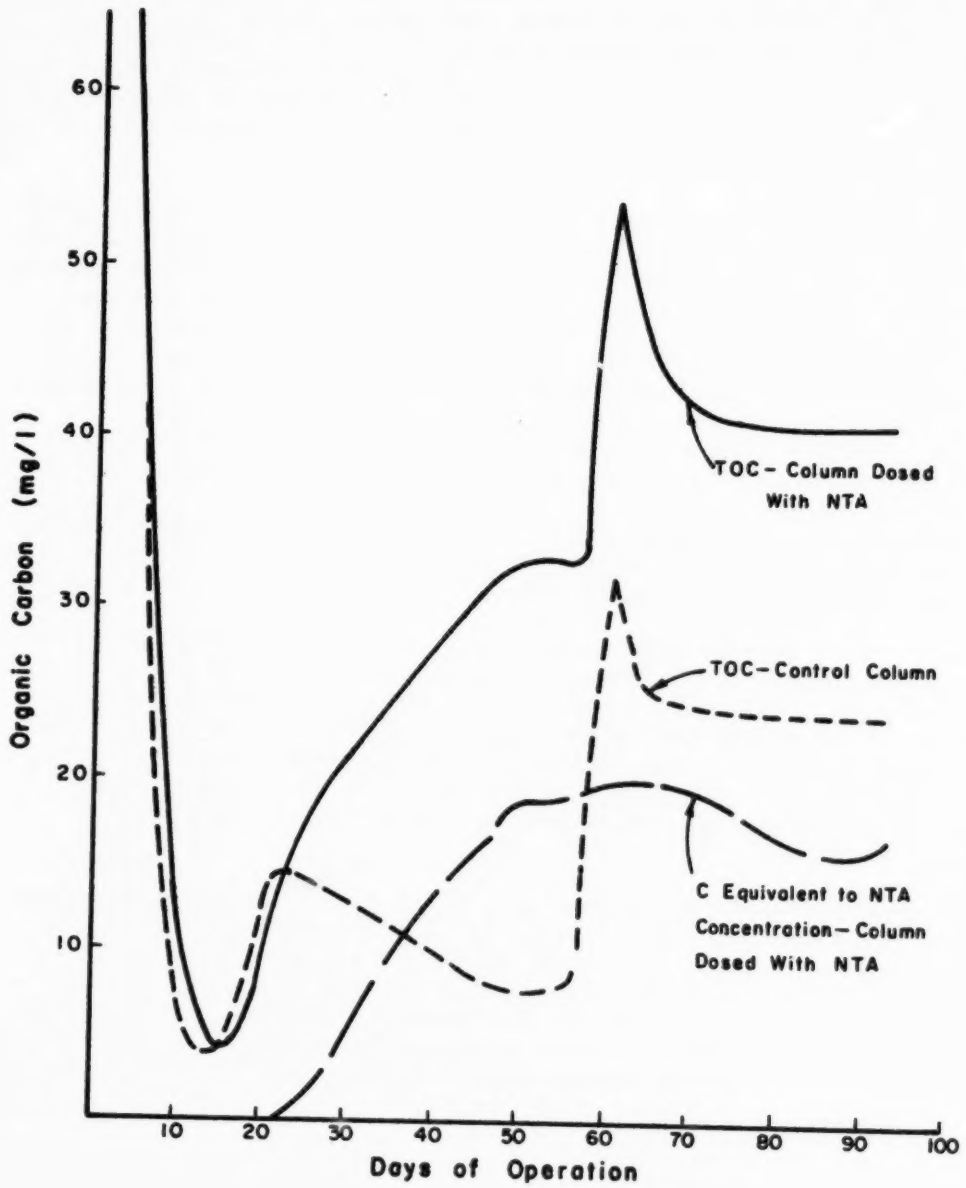


FIGURE 15. ORGANIC CARBON IN EFFLUENTS FROM SATURATED SAND-METALS SLUDGE COLUMNS

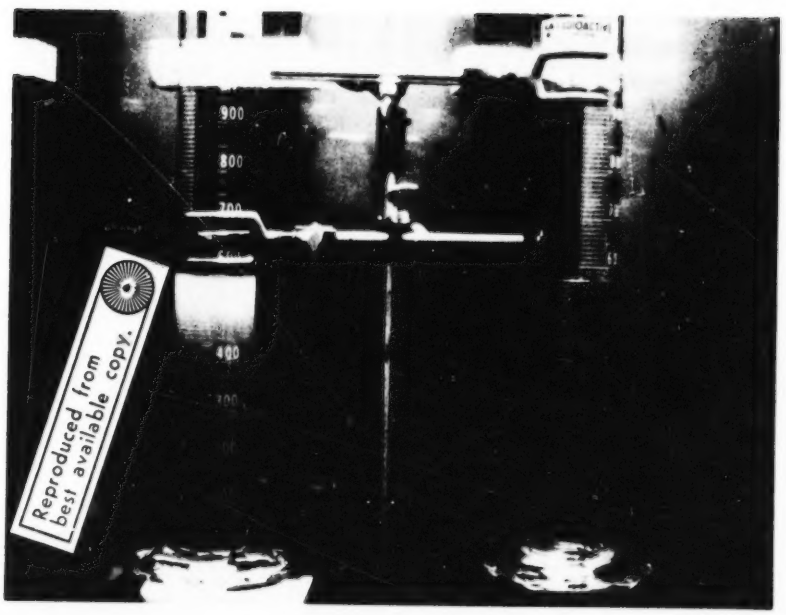


FIGURE 16. VISUAL COMPARISON OF EFFLUENTS FROM SATURATED SAND-METALS SLUDGE COLUMNS DOSED WITH FEEDS WITH AND WITHOUT NTA

include the quantities of various metals in the soil, the anionic species with thich the metals are associated in the soil matrix, the concentration of NTA in the infiltrating solution and the relative stabilities of the various metal-NTA complexes under conditions prevailing in the particular saturated soil system of concern.

For example, cadmium was eluted in considerable quantity from the saturated sand-metals sludge column, but appeared only in very low quantity in the effluent from the sand-metal ores column, apparently because it was present as the hydroxide in the sludge column and as the sulfide in the ores column. Also, cadmium and iron apparently formed the most stable complexes with NTA of any of the metals determined under conditions prevailing in the saturated

sand-metals sludge column, and hence appeared in greatest quantity in the effluent from this column. Zinc, chromium, lead, and mercury in this column almost certainly were also chelated by NTA as indicated by their appearance in low levels in the effluent with maximum concentrations generally corresponding to maximum NTA levels. However, the stabilities of these chelates under conditions in the column were such that most of the NTA was involved in formation of chelates with cadmium, iron, and possibly other metals not determined in this study. Had cadmium been present in lower concentration or not present at all in this column, or had conditions prevailed in the column under which the cadmium-NTA complex was less stable, such as a different pH, one or more of the other metals likely would have appeared in high concentration in the effluent.

One of the objectives of this second series of soil column studies was to gain further information concerning the possibility that metals in unsaturated soil systems might be leached into ground waters as a result of initial solubilization by infiltrating NTA, with the metals remaining in solution and moving on into the underlying ground water even though the NTA portion of the metal-NTA chelate was rapidly degraded subsequent to chelate formation. No definitive information was obtained concerning this possibility because only partial degradation of NTA occurred in the unsaturated column of sand enriched with metals sludge. However, these studies did point out that infiltration of water containing NTA through unsaturated soils, containing high levels of heavy metals, could result in both NTA and metals entering the underlying ground water because of metals toxicity and the resulting inhibition of microbial degradation of NTA.

Overall, these studies appear to indicate a potential for pollution of ground water by heavy metals in situations where NTA might infiltrate through soil systems containing high levels of metals such as cadmium, zinc, chromium, lead, and mercury. Introduction of NTA from detergents into waste lagoons which have been receiving metals plating wastes would appear to be a situation of particular concern.

Simulated Aquifer Studies

Figures 17 and 18 graphically depict the data from simulated aquifers employed to investigate the possible degradation of NTA in an essentially anaerobic ground-water environment.

As shown in Figure 17, concentrations of 30-32 mg NTA/Na_3/l at the beginning of aquifer operation decreased to essentially zero in a period of 52 days in the aqueous phases of both Aquifer Number 2, which contained NTA uniformly labeled with ^{14}C, and Aquifer Number 1 which contained only nonlabeled NTA, while the level of ^{14}C in Aquifer Number 2 decreased approximately 40 percent from about 560 pCi/ml to 330 pCi/ml. During this same 52-day period of operation NTA Na_3 in the sterile control aquifer decreased from approximately 33 mg/l to 29 mg/l, with ^{14}C in this unit showing an even smaller decline.

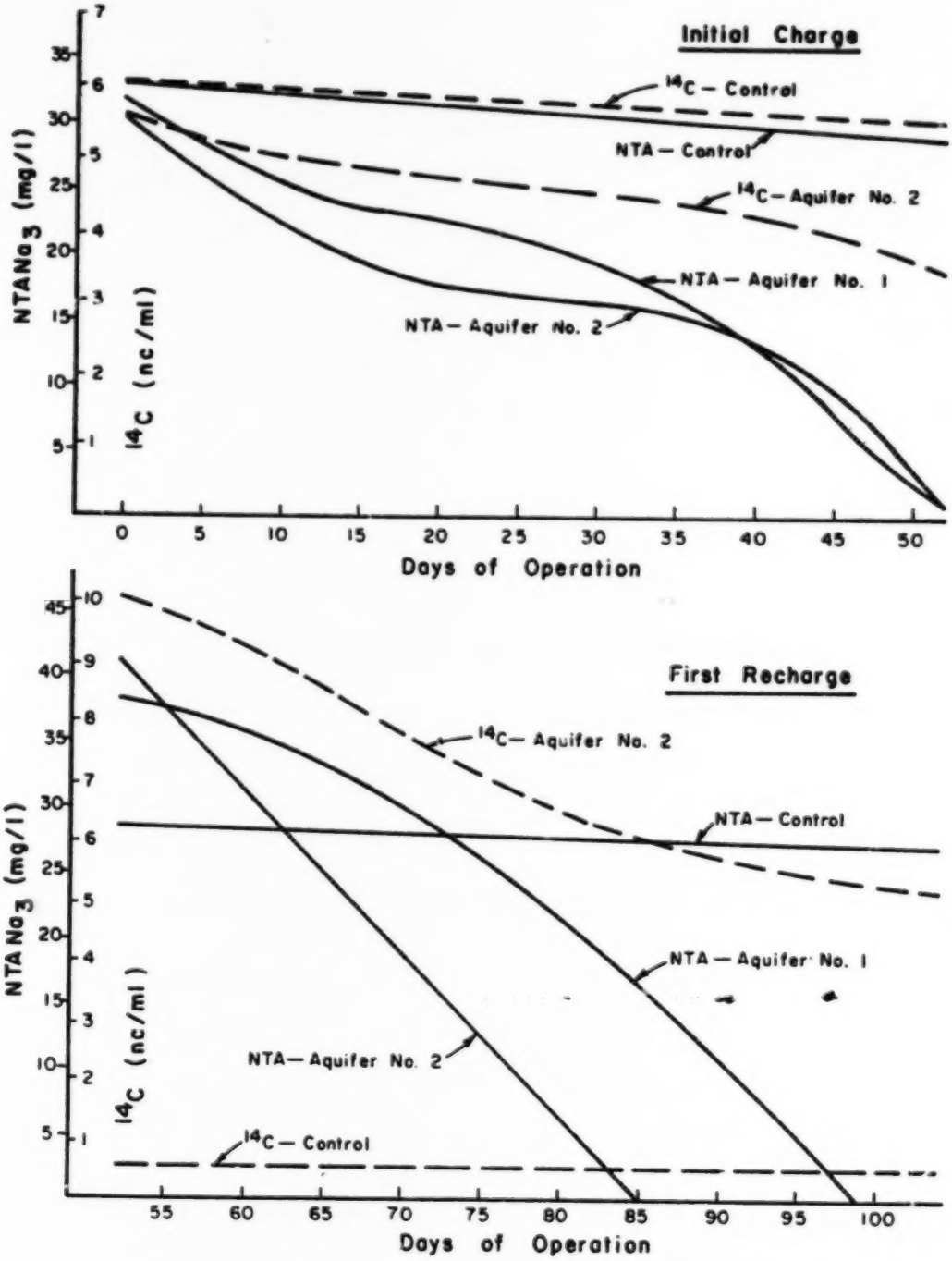


FIGURE 17. DEGRADATION OF NTA IN SIMULATED AQUIFERS; INITIAL CHARGE AND FIRST RECHARGE.

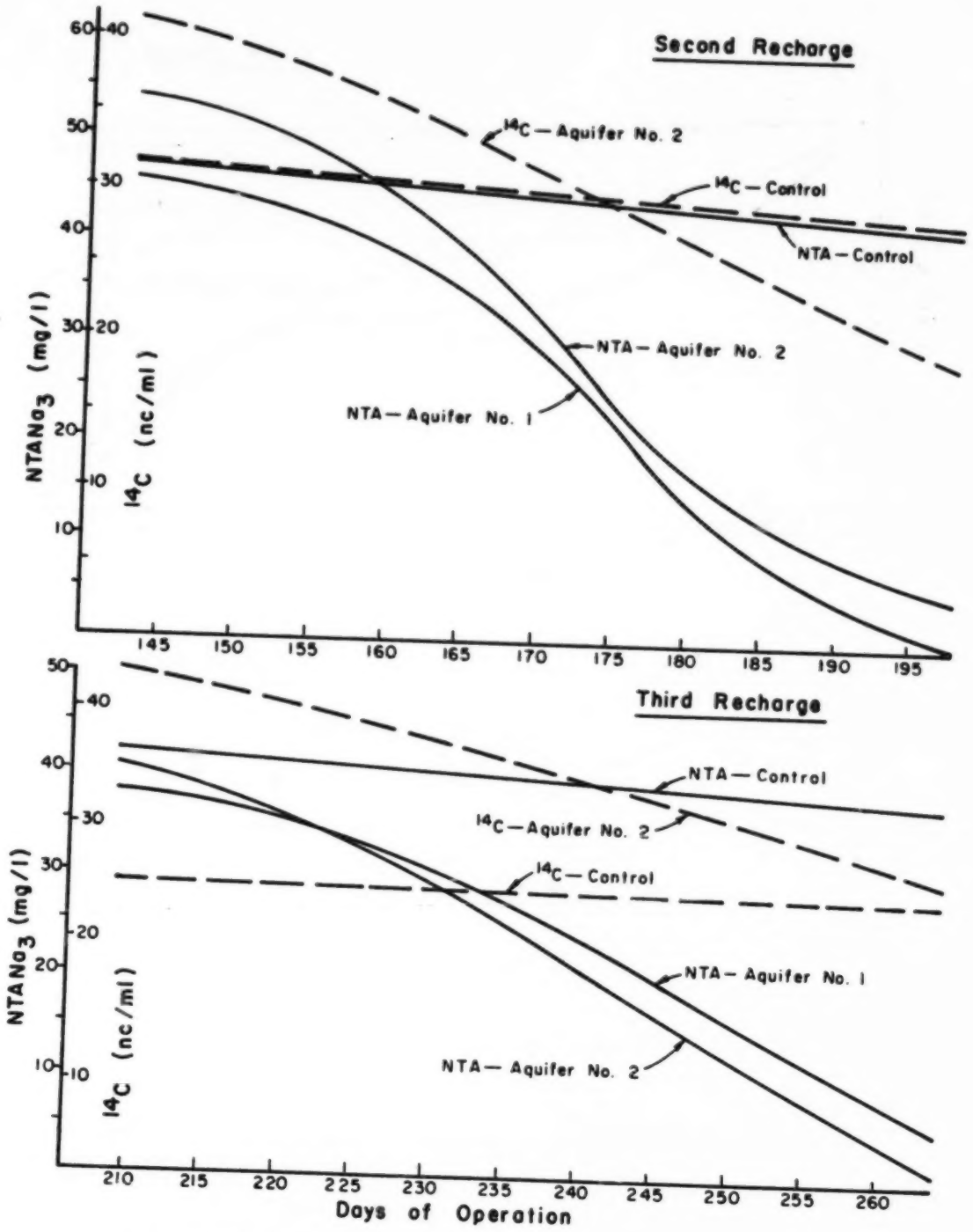


FIGURE 18. DEGRADATION OF NTA IN SIMULATED AQUIFERS; SECOND AND THIRD RECHARGES.

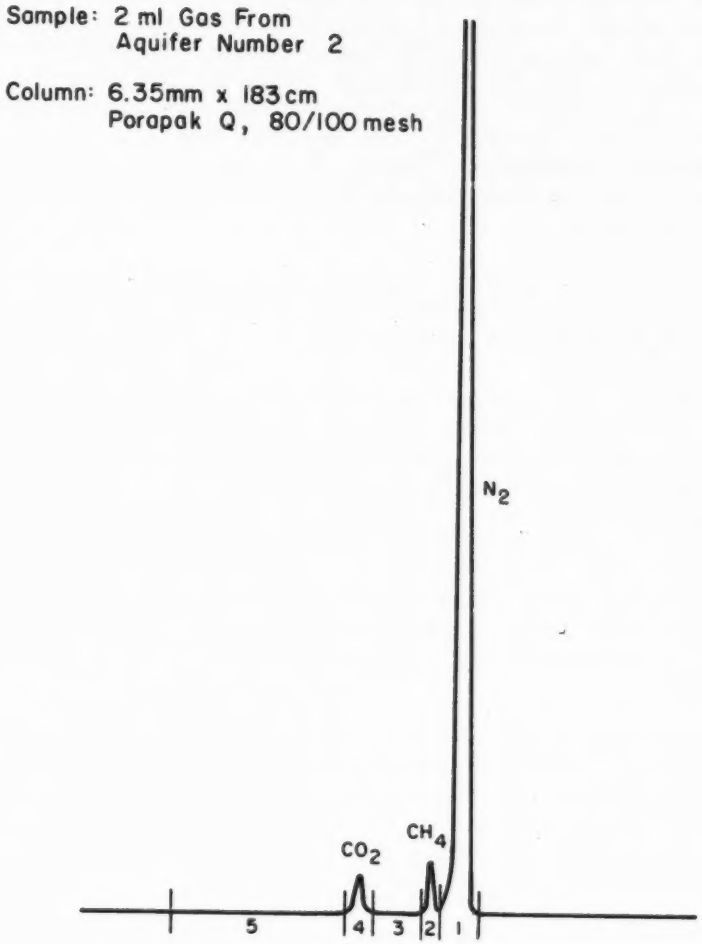
These data indicated beyond reasonable doubt that significant microbial degradation of NTA had occurred in the experimental simulated aquifers during this initial 52-day period of operation. However, occasionally during this period gas samples taken from the aquifer systems were shown by gas chromatography to contain low levels (usually less than 0.2 percent) of oxygen, probably as a result of problems with liquid sealed pressure relief systems which were employed on the aquifers early in the study but which were subsequently abandoned. Hence, there was some doubt concerning the role of oxygen in the observed degradation of NTA during the initial period of aquifer operation.

Results obtained when the simulated aquifers were recharged with additional NTA Na_3 on the 52nd and 143rd days of operation served to further clarify the nature of NTA degradation in these units.

In the period following the first recharging (Figure 17), degradation of NTA was observed to occur at higher overall rates than in the initial period of operation, with initial concentrations of 38 mg NTA Na_3/l in Aquifer Number 1 and 41 mg NTA Na_3/l in Aquifer Number 2 declining to zero in 47 and 33 days, respectively. Following the second recharging, the aquifers were operated under a nitrogen blanket to further preclude the possibility of diffusion of oxygen into the units through tubing and septa. An initial concentration of 46 mg NTA Na_3/l in Aquifer Number 1 was completely degraded in 55 days, while a concentration of 54 mg NTA Na_3/l initially present in Aquifer Number 2 was reduced to 5 mg/l in the same period (Figure 18).

Gas samples obtained from the simulated aquifers during the periods of operation following the first and second rechargings were shown by gas chromatographic analyses to contain essentially no oxygen. These same analyses also revealed the production of methane and low levels of carbon dioxide in both experimental aquifers during these periods, with no production of either gas in the control aquifer.

Anaerobic degradation of NTA in the simulated aquifers was indicated beyond reasonable doubt by confirmation of the methane produced in Simulated Aquifer Number 2, which contained ^{14}C labeled NTA, as a degradation product of NTA. This was accomplished by fractionation of aquifer gas samples by chromatography on a 6.35 mm x 183 cm Porapak Q column, with passage of successive fractions of effluent gas from the chromatograph through 16 ml aliquots of toluene scintillation cocktail and subsequent determination of the radioactivity of these aliquots by liquid scintillation spectrometry. A typical analysis is presented in Figure 19. As this figure shows, the carbon dioxide in the aquifer gas was also an NTA degradation product, as would be expected. Since the toluene scintillation cocktail was undoubtedly not efficient in scavenging the radioactive methane and carbon dioxide from the gas chromatography effluent, the activities shown in Figure 19 probably are indicative of much higher actual activities of the gases produced in the aquifer.



Fraction	Radioactivity (CPM)
1	38.8
2	364.8
3	39.8
4	465.9
5	41.4
Blank	38.4

FIGURE 19. DETECTION OF RADIOACTIVITY IN GASES FROM A SIMULATED AQUIFER.

Thin-layer chromatography and radioautography of water samples obtained from Simulated Aquifer Number 2 during the periods of operation following the first and second rechargings clearly showed the progressive disappearance of NTA from this unit after recharging. However, there was no evidence for the presence of any of the postulated degradation products of NTA listed in Table 2 at any time during these periods of operation. Radioautograms did provide some evidence for the presence in this aquifer during degradation of ^{14}C-labeled NTA of at least one unknown radioactive compound with R_f values very similar to those of NTA in the chromatographic systems employed. This substance was most noticeable in radioautograms of samples obtained during maximum degradation of NTA following the second recharge of Aquifer Number 2. It appeared to have corrected R_f values of 0.43 and 0.34, respectively, when chromatographed using the CG-400 resin-Avicel SF-0.15 N NaCl system and the Avicel SF-tBFW system, while the corresponding R_f values for NTA using these systems were 0.38 and 0.41. Time limitations precluded further investigation and characterization of this possible anaerobic degradation product of NTA. The chromatographic properties of this substance were so similar to those of NTA that the possibility of its being a chromatographic anomally, produced by the effect on NTA of salts or other substances in the sample solutions, cannot at present be eliminated.

Radioautograms of water samples obtained from Aquifer Number 2 after all of the NTA had disappeared (as indicated by the zinc-zincon procedure) revealed no radioactive products other than very low quantities of substance at R_f values similar to those of NTA. This material was sufficient to account for only a small portion of the carbon-14 still present in the aqueous phase of the aquifer at this time (Figure 17). Although a portion of this ^{14}C must have been present in the form of carbon dioxide and methane, it would appear likely that other volatile degradation products, which would have been lost during sampling and chromatography and hence would not have been detected by radioautography may have been present in the aqueous phase of the aquifer after all of the NTA had been degraded.

Figure 18 shows that degradation of NTA proceeded readily in both of the experimental aquifers after the third recharging, which included Sego as a carbon source in addition to NTA. As shown by both this figure and Table 3, overall rates of NTA degradation in the two simulated aquifers following this recharge were somewhat less than the rates following the first two rechargings. The magnitudes of these rate decreases were relatively small, however, and the extent to which they were attributable to the extraneous carbon source is open to question. Products of microbial metabolism, accumulating in the aquifers during the 210 days of operation prior to the third recharge, could also have caused some decrease in NTA degradation. It should be noted that addition of an extraneous carbon source to an aquifer with the initial charge of NTA, before the microbes present in the aquifer have adapted to degrade NTA, could produce a quite different effect than observed here. There was, however, no opportunity to conduct such an experiment during these studies.

Table 3

Summary of NTA Data for Simulated Aquifer Studies

Operational Period	Aquifer	NTA Na_3 (mg/l) Start	Finish	Decrease	Days of Operation	Mean Rate of Degradation (mg/l/day)
Initial Charge	1	32	0	32	52	0.615
Initial Charge	2	30	0	30	52	0.577
Initial Charge	Control	33	29	4	52	0.077
First Recharge	1	38	0	38	47	0.809
First Recharge	2	41	0	41	33	1.241
First Recharge	Control	29	27	2	53	0.038
Second Recharge	1	46	0	46	55	0.836
Second Recharge	2	54	5	49	55	0.891
Second Recharge	Control	48	43	5	55	0.091
Third Recharge	1	38	5	33	55	0.600
Third Recharge	2	41	2	39	55	0.710
Third Recharge	Control	42	38	4	55	0.073

Overall, the data obtained in the simulated aquifer studies indicated that NTA entering an essentially anaerobic ground-water environment will probably undergo degradation. This phenomenon could be quite important in retarding the development of high levels of NTA in aquifers receiving waste waters containing this substance and in decontamination of aquifers which might become polluted by NTA. These studies also indicate that the final products of NTA degradation within an aquifer will likely consist mostly of methane, carbon dioxide, and probably other volatile materials. Further investigation is needed to determine if possibly deleterious organic products might be generated during such degradation.

The sand employed for construction of the simulated aquifers in these studies was obtained from a very shallow natural aquifer which probably contained a numerous and active population of anaerobic microorganisms because of periodic infusion with water of relatively high organic content. This, as well as retention time, probably explains the differences in the extent of NTA degradation in the simulated aquifers and the previously described saturated soil columns. The soil columns were constructed from well aerated soils that were necessarily processed in preparation for packing in a manner likely to result in destruction of any anaerobic microorganisms that might be present. It is also likely that many natural aquifers would have anaerobic microbial populations much less numerous and active than the population present in the aquifer providing the sand used in these studies. Hence, the degradation of NTA, or at least the initiation of such degradation, would be likely to occur much more slowly in many natural aquifers, particularly deep aquifers, than was observed in these studies.

SECTION VI

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A project of this nature necessarily involves the energy and talent of a number of people to whom proper credit should be given.

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Linda Harmon is acknowledged with thanks for designing the computer program used in analyzing project data and for somehow managing to type various drafts of the report while meeting all deadlines.

The assistance of Richard E. Thomas, who provided invaluable advice in regard to soil column preparation and operation, and of Jack W. Keeley, who was responsible for a significant portion of the initial project planning and provided assistance and encouragement throughout the investigations, is gratefully acknowledged.

SECTION VII

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27 Abstract

Laboratory studies were employed to investigate the fate and effect of NTA both in ground waters and in soil profiles overlying ground waters.

Studies of the sorption of NTA by sand, loam, and clay-loam soils indicated that sorption of NTA on soils could slow its movement into and through ground waters. Sorption will probably not be sufficient to prevent or greatly reduce potential pollution of ground water by NTA used as a detergent builder.

Soil column studies were employed to investigate the degradation and effect on metals of NTA infiltrating through soils. These studies indicated: NTA infiltrating through most unsaturated soils likely would undergo rapid and complete degradation and contribute only inorganic nitrogen compounds and carbonate to ground waters; NTA infiltrating through saturated soils would probably experience only very limited degradation, with a major portion entering ground water intact; any NTA which escaped degradation during infiltration through soils could transport such metals as iron, zinc, chromium, lead, cadmium, and mercury from soils into ground waters.

Studies with model aquifers constructed from natural aquifer sand indicated that NTA would likely undergo slow degradation in essentially anaerobic ground-water environments, with production of CO_2, CH_4, and possibly other organic compounds.

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